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OF THE USSR

(ZHURNAL ANALITICHESKOI KHIMII)

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION II. THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF PALLADIUM*

Iu. A. Bankovskii and A. F. Ievin'sh

Institute of Chemistry, Academy of Sciences, Latvian SSR, Riga

Of a fairly large number of color reactions which have been described in the literature for palladium, only a few of them have been studied in sufficient detail.

The ease with which palladium is reduced to the elemental state, and the formation, during this reduction, of intensely colored colloidal solutions, have served as the basis for developing a number of methods for detecting and determining palladium [1-7]. Some methods are based on measurement of the optical density of colored complexes of palladium [8-13]. Because of their comparatively low sensitivity, these methods are only suitable for the determination of considerable amounts of palladium.

Methods which are based on the use of organic reagents would seem to be more promising. The reagents most widely used are those which contain the p-nitrosophenylamino group which is characteristic for palladium.

Of this class of reagents, the ones which have found widest application are p-nitrosodiphenylamine [14-15] and p-nitrosodimethylaniline [16-17]. The big disadvantage of these reagents is the effect of neutral salts on them, and the necessity of carrying out a preliminary removal of palladium from Fe, Ni, Co, Cu, Ir, Rh and other elements. For the photometric determination of palladium the following reagents have also been recommended: thiourea [18], 2-mercapto-4,5-dimethylthiazole [19], β-furfuraldoxime [20], α-nitroso-β-naphthol [21], Complexon III [22], methylglyoxime; dimethylglyoxime, salicaldoxime, β-hydroxynaphthaldoxime [23], etc. A review of photometric methods of determining palladium has been given in the paper by Beamish and McBryde [24].

The following reagents have been suggested for the gravimetric determination of palladium: α-furildioxime [25, 26], violuric acid [27], 3-hydroxy-1,3-diphenylhydrazine [28], 4-isopropyl-1,2-cyclohexane-dioxime [29], thiobarbituric acid and phenylthiourea [30], dimethylglyoxime [31-33], α-benzoinoxime and β-furfuraldoxime [25], methylbenzoylglyoxime [31], and diethyldithiophosphoric acid [34].

Fuller information on the methods used for the qualitative and quantitative determination of palladium is to be found in a number of reviews [35, 36].

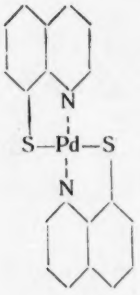
Thiooxime (8-mercaptoquinoline) is a highly specific reagent for palladium; this reagent, under certain conditions, permits the determination of palladium in the presence of other elements; it interacts with divalent palladium ions to form a bright-red 8-mercaptoquinolate (thiooxinate) of palladium which is insoluble in water, the formula of this compound is $Pd(C_9H_6NS)_2 \cdot H_2O$; it is soluble in various organic solvents to give solutions with an intense rose or orange color [37].

The best extractants for palladium thiooxinate are chloroform, chlorobenzene, and bromobenzene. Palla-

*Communication I, see J. Anal. Chem. 13, 267 (1948).

dium thiooxinate is less soluble in carbon tetrachloride, diethyl ether, amyl acetate, and carbon disulfide, while it is completely insoluble in aliphatic hydrocarbons.

The ready solubility of palladium thiooxinate in most organic solvents, the high color intensity of these solutions, and the high stability toward acids, give a basis for assigning the structure of an inner-complex salt to this compound.



In accordance with current ideas on the properties of organic reagents of the type R—SH [38], and in view of the presence of a favorable atomic group in the thiooxine molecule, one can postulate the formation of a highly-stable five-membered ring during the interaction of palladium with thiooxine, in which the palladium, while substituting the hydrogen of the mercapto group, is simultaneously connected through a coordination bond with the nitrogen of the pyridine nucleus of quinoline. Palladium thiooxinate possesses a very high stability.

Fifty γ of palladium in the form of an aqueous solution (5 ml) was introduced into a separating funnel, followed by 40 ml of a buffer solution of a definite pH, and 4 ml of a 5% alcoholic solution of thiooxine. The palladium thiooxinate was extracted with 10 ml of chloroform by vigorous shaking for 3-4 minutes. The chloroform extract was filtered through a plug of cotton wool and the color measured in a 1 cm cell in a Pulfrich photometer. The amount of palladium extracted was then determined by means of a calibration curve (in weakly acid solutions) constructed beforehand.

As is evident from Fig. 1, complete extraction of palladium thiooxinate is observed from strongly acid (4 N HCl) solutions. Palladium thiooxinate is also completely extracted from strongly alkaline solutions.

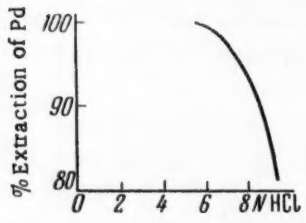


Fig. 1. Extractability of palladium thiooxinate as a function of the acidity of the medium.

It is clear from Fig. 2, that there are three maxima on the absorption curve for a solution of palladium thiooxinate in chloroform, these maxima are at 272 mμ, 286 mμ, and 485 mμ. The molar extinction coefficients of palladium thiooxinate were found to be E_{272} = 43,500; E_{286} = = 39,200, and E_{485} = 7,750. Thus, the highest sensitivity is observed at 272 mμ and also at 286 mμ.

In the work described here, quantitative determination of palladium was carried out in the visible part of the spectrum using a Pulfrich photometer.

As Fig. 3 shows, extracts of palladium thiooxinate in chloroform conform to the Lambert – Beer law up to concentrations of 27 γ/ml (6 N HCl).

More than 5-6 γ of Pd can be determined on a Pulfrich photometer. A spectrophotometer set at 485 mμ permits the determination of as little as 2 γ Pd in the test solution.

Thiooxine, as a reagent which contains the sulfhydryl group, should, according to current ideas [38], react in aqueous media only with those elements which form sulfides which are stable in the presence of water. As a consequence of this, even very high concentrations of the alkali, and the alkaline-earth metals, as well as Al, Ti, Zr, Hf, Th, Cr, etc. do not interfere with determination of palladium. In strongly acid solutions (6 N HCl), in the presence of thiourea (for masking Os, Ru, Pt, Cu, Ag, Au, and Hg) thiooxine is a special reagent for palladium.

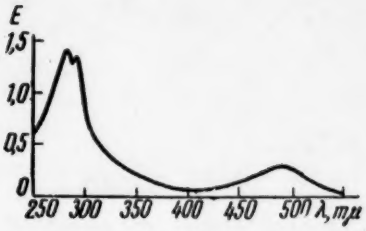


Fig. 2. Absorption spectrum of a 0.000033 M solution of palladium thiooxinate in chloroform (cell 1 cm). Taken on a SF-4 spectrophotometer.

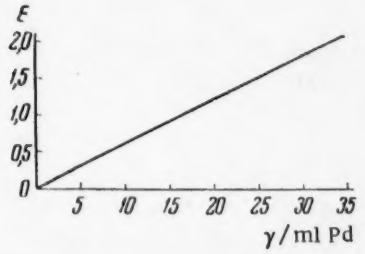


Fig. 3. Conformity of chloroform solutions of palladium thiooxinate to the Beer law (Pulfrich photometer, spectrofilter S-47).

Pt, Os, and Ru react with thiooxine in fairly acid solutions also, and, in rather overwhelming amounts (with respect to palladium), lead to high results for palladium. Platinum in amounts of 20 mg, and osmium and ruthenium in amounts of 1-2 mg, can be masked with thiourea. Iridium and rhodium do not react with thiooxine in strongly acid solution. We have successfully determined Pd (20 γ) in the presence of 2 mg of Rh and 10 mg of Ir. The effect of higher concentrations of Rh and Ir has not been studied.

The effect of the following elements has also been studied: Fe, Co, Ni, Ag, Au, Hg, Zn, Cd, Pb, Mn, Tl, Sn, W, Mo, Sb, Bi, U, As and Ge. With the exception of molybdenum, these elements do not interfere with determination of palladium, even when they are present in amounts which are far greater than that of palladium.

Trivalent iron does not interfere with palladium determination in 6 N HCl when the iron is present in amounts up to 80 mg. Larger amounts (up to 200 mg) can be reduced by sodium hyphophosphite or some other suitable reducing agent (in dilute solutions palladium is not reduced to the metal by hypophosphite) and can be masked by addition of 15 ml of a saturated solution of oxalic acid.

Cu, Hg, Ag, and Au (just like Ru and Os) react with thiooxine in strongly acid solutions. The thiooxinates of Ag and Au are not extracted by organic solvents and do not interfere with palladium determination. When, however, very large amounts of copper are present, some may pass into the extract. Accordingly, Cu like Hg, Ag, and Au (the bulky thiooxinates of which, although insoluble in chloroform, still interfere with the separation of the extract from the aqueous phase) must be masked with thiourea. When thiourea is used for this purpose, 50 ml of test solution (6 N HCl) should not contain more than 2 ml of a 8% solution of thiourea.

In the presence of more than 5-6 mg of Hg, Ag, and Au, the thiooxinates of these elements are precipitated, and though they are not extracted by organic solvents, they still interfere with the separation of the extract from the aqueous phase. In this case, after the extraction has been carried out in a separating funnel, 5-10 ml of a 8% thiourea solution is added, and the whole shaken up. The thiooxinates of these elements thereupon dissolve and the chloroform extract is readily removed.

In the presence of more than 0.5 mg of univalent mercury and divalent tin, low results are obtained for palladium.

Molybdenum (> 20 γ) is the only element that can cause serious difficulties. In the presence of large amounts of molybdenum, it is possible to utilize the lower stability of its thiooxinate as compared with that of palladium, and it can be washed out of the chloroform extract with hydrochloric acid. When 5 mg of molybdenum is present, the extract has an intense brown color. This brown extract is transferred to another separating funnel in which it is shaken up with 60 ml of 8 N HCl for 5-7 minutes. When this is done, the molybdenum thiooxinate is broken down and the chloroform extract assumes the pure rose color of palladium thiooxinate. When 5-7 minutes extraction by vigorous shaking is not sufficient to remove the last traces of brown color, the extract is shaken up once again with another 60 ml lot of 8 N HCl. The extract is then filtered and the extinction measured; palladium is then determined by means of the calibration curve.

There is still one more limitation to the given method for palladium. It is desirable that no oxidizing agent be present. In principle, oxidizing agents do not prevent determination of palladium, but, by oxidizing the thiooxine, they may lead to low results during palladium determination. In view of the high hydrochloric acid concentrations used in the method, the presence of appreciable amounts of nitrates in the test solution is inadmissible. It is best to reduce vanadate to vanadyl, trivalent iron to the ferrous state, etc. This is, however, not obligatory, since thiooxine itself is a reducing agent, and all that will happen in such cases is that more of the thiooxine will be used up.

Determination of Palladium in the Presence of Various Elements (20 γ Pd taken)

Foreign element (Me), in mg	Ratio $\frac{Pd}{Me}$	Pd found, in γ	Foreign element (Me), in mg	Ratio $\frac{Pd}{Me}$	Pd found, in γ
Pt^{IV} — 20	1 : 1000	21	Ge^{IV} — 100	1 : 5000	21
Os^{VIII} — 2	1 : 100	20	Mn^{II} — 560	1 : 2800	19
Ru^{III} — 1	1 : 50	21	Tl^{I} — 70	1 : 3500	20
Rh^{III} — 2	1 : 100	19	As^{III} — 100	1 : 5000	18,5
Ir^{IV} — 10	1 : 500	19,5	As^{V} — 100	1 : 5000	19,5
Cu^{II} — 5	1 : 250	21	Sb^{III} — 50	1 : 2500	21
Ag — 20	1 : 1000	19	Bi^{III} — 50	1 : 2500	21
Au^{III} — 100	1 : 5000	18	Pb — 250	1 : 12500	20
Hg^{II} — 100	1 : 5000	20	Sn^{IV} — 0,5	1 : 25	19
Fe^{II} — 200	1 : 10000	20,5	Se^{IV} — 20	1 : 1000	21,5
Fe^{III} — 80	1 : 4000	21	W^{VI} — 100	1 : 5000	19
Ni — 160	1 : 8000	20	Mo^{VI} — 0,02	1 : 1	22
Co^{II} — 250	1 : 12500	20	U^{VI} — 500	1 : 25000	20
Cd — 400	1 : 20000	20	V^{IV} — 80	1 : 4000	21
Zn — 100	1 : 5000	18,5			

On the basis of numerous experiments a method which is described below has been developed for the determination of palladium. A very large excess of thiooxine (250 mg) with respect to the amount of palladium to be determined is necessary in order to lower the dissociation of palladium thiooxinate at the high acidity used, and in order to ensure its complete extraction. At lower hydrochloric acid concentrations, for example 3 N HCl, it is possible to use only 2 ml of a 4-5% solution of the reagent. For 100% extraction of palladium from 2 N HCl only a very small excess of reagent is necessary. But, at low acidities, a large number of foreign elements interfere.

Analytical Procedure. To not more than 20-25 ml of test solution contained in a separating funnel is added the same volume of concentrated hydrochloric acid, 1.5 ml of 8% thiourea solution, and 5 ml of a 4-5% solution of thiooxine in 6 N hydrochloric acid. Palladium thiooxinate is extracted with 10 ml of chloroform by shaking with the latter for 5 minutes. The extract is removed and filtered through a cotton wool plug: the light absorption of the filtrate is measured in a 1 cm cell in a Pulfrich photometer using a S-47 filter, or on the SF-4 spectrophotometer at 485 mμ. The amount of palladium is then determined by means of a calibration curve constructed under the same conditions using pure solutions of palladium.

When large amounts of iron are present, it should be masked as described above. When more than 20 γ of molybdenum is present it should be subjected to the washing treatment described above.

SUMMARY

1. Paladium thiooxinate $Pd(C_9H_6NS)_2 \cdot H_2O$ is stable in strong acid solutions, and is readily extracted by most organic solvents to give solutions with an intense rose color.

2. A highly specific photometric method has been developed for the determination of palladium (5-270 γ) in the presence of considerably larger amounts of foreign elements such as: Pt, Os, Ru, Rh, Ir, Cu, Ag, Au, Hg, Fe, Ni, Co, Zn, Cd, Ge, Mn, Tl, As, Sb, Bi, Sn, Se, W, Mo, Pb, U, V, etc.

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SEPARATION OF THORIUM FROM TITANIUM, ZIRCONIUM, AND OTHER ACCOMPANYING ELEMENTS BY THE HOMOGENEOUS PRECIPITATION METHOD

F. V. Zaikovskii and L. I. Gerkhardt

The homogeneous precipitation method* has found practical application in analytical chemistry for the determination of calcium [1], barium [2-3], strontium [4-5], lead [6], tin [7], copper and silver [8], thorium [9-11], rare earths [12], nickel and cobalt [8], metals of the hydrogen sulfide group [13-17], and some others. The advantage of this method as compared with ordinary precipitation is well known.

The compounds used as reagents are nonionized compounds which, under conditions leading to hydrolysis, dissociation, or breakdown of complex organic molecules to more simple compounds, supply precipitant ions. Crystallization "centers" (precipitation) are uniformly distributed through the whole volume of the solution. Of the huge number of organic materials which are capable of supplying precipitant ions in solution, few as yet have found application. In particular, methyl- and ethyl oxalates [10, 20] and compounds yielding iodate ions [21] have been suggested for precipitation of thorium. Quantitative separation of thorium as the oxalate in cases where other metal ions are present, is a difficult problem. Thorium oxalate may be obtained either in a gelatine-like form or in the form of coarse crystals [22] depending on precipitation conditions.

For the quantitative determination of thorium it is important to get a precipitate in the form of large crystals; this can be achieved by the homogeneous precipitation method [10].

The reagent which we used for this purpose was acetonedioxalic acid; this was prepared by the condensation of acetone with oxalic acid [23].

$$CO(CH_3)_2 + 2H_2C_2O_4 \rightleftharpoons CO(CH_2COCOOH)_2 + H_2O.$$

Acetonedioxalic acid in aqueous solution provides a precipitant for thorium—the oxalate ion. In aqueous-acetone media the extent of the coprecipitation of accompanying elements decreases, this has been shown to be true in many instances of the precipitation of metal ions from aqueous-organic media [18, 24]. Acetonedioxalic acid should provide large excess amounts of oxalate ions. A large excess of oxalate decreases the extent of the coprecipitation of zirconium and titanium [22], and lowers the solubility product of thorium oxalate [25].

Preparation of a solution of acetonedioxalic acid. Oxalic acid (150-200 g) is dried at 90-100° for 4 hours, after which it is ground, and drying continued for a further 1.5 hours; 40 g of the dried oxalic acid is dissolved in 100 ml of anhydrous acetone (b. p. 56°). The reagent is used on the day following preparation. 15 ml of reagent supplies about 4 g of oxalate ions.

Precipitation of thorium as the oxalate by means of acetonedioxalic acid. Precipitation of thorium as its oxalate has been studied by many authors [21, 22, 26, 27]. Quantitative precipitation of thorium oxalate occurs at a terminal pH of 0.5-2.0 and in the presence of a large excess of oxalic acid; the latter, in addition, decreases

*A. P. Terent'ev and co-workers [18] have suggested the term "the method of in situ nascendi reagents" for such a precipitation. Other authors [9] have called this method "indirect precipitation."

the amount of coprecipitation of zirconium and titanium. The presence of a coprecipitant (calcium ions) in solution is essential, since this ensures complete separation of thorium and the rare earths. In the presence of large amounts of foreign ions, and particularly of iron, aluminum, zirconium, and titanium, small amounts of thorium are not quantitatively precipitated as the oxalate. Precipitation of thorium as the oxalate takes 15-18 hours. The presence of other compounds (ammonium salts, phosphates, etc.) in solution prevents quantitative separation of thorium oxalate.

Separation of thorium by means of acetone dioxalic acid in relation to the pH of the solution was investigated as follows.

To 50 ml of solution containing 96.7 γ of thorium, at various pH values indicated in Table 1, 7 ml of acetonedioxalic acid solution was added, and the mixture boiled for 15 minutes. On the following day the precipitate of thorium oxalate was filtered through a "white band" filter paper 7 cm in diameter, and the precipitate washed 2-3 times with 1% oxalic acid; it was then dried and calcined in a 5-6 ml porcelain crucible. The residue was fused with 0.8 – 1 g of sodium peroxide. After cooling, the melt was dissolved on heating in 25 ml of water, the solution was then filtered through a 7 cm diameter "white band" filter paper, and washed 3-4 times with water. The thorium hydroxide on the filter was dissolved in hot 0.09 N hydrochloric acid, and thorium determined by means of arsenazo [28], using a method published previously [29].

TABLE 1

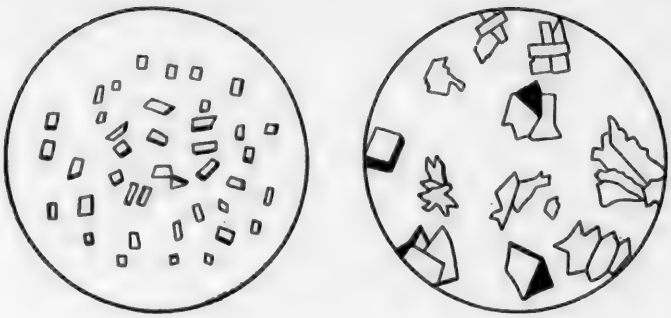
Precipitation of Thorium as Its Oxalate from a Homogeneous Solution (96.7 γ of Th taken)

pH at the end of the precipitation	Th found, in γ	Error in Th, γ	pH at the end of the precipitation	Th found, in γ	Error in Th, γ	pH at the end of the precipitation	Th found, in γ	Error in Th, γ
0.3	71.7	– 25.0	1.5	91.0	–5.7	2.1•	99.0	+1.3
0.6	93.7	– 3.0	1.6	82.0	–14.7	2.6•	97.0	+0.3
0.7	91.2	– 5.5	2.2	58.5	–38.2	3.0•	78.0	–18.7
1.1	91.2	– 5.5	2.6•	100.0	+ 3.3			

•25 mg of Ca^{2+} was added as coprecipitant.

It is clear from Table 1 that thorium is quantitatively precipitated as the oxalate from homogeneous solution at a pH of 0.6-1.5; when the pH is increased, precipitation is incomplete. When a coprecipitant is present—calcium ions—thorium is quantitatively precipitated even at pH 2.62. Microcrystalloscopic examination of thorium oxalate obtained by the homogeneous precipitation method (Fig. 1), and that obtained by the normal oxalate method (Fig. 2), showed that in both cases the crystals are obtained in the form of rectangular tetragons, and sometimes in the form of rhombs; in the case of those obtained by homogeneous precipitation, however, the crystals fuse into each other and larger crystals are obtained with clearly defined edges.

Separation of thorium from zirconium, titanium and other elements. Separation of small amounts of thorium from foreign elements does not proceed quantitatively when the normal oxalate method is used. A method which has been adopted is to separate thorium beforehand as its insoluble fluoride [22, 30], this procedure also separates thorium from zirconium, titanium, niobium, tantalum, and some other elements. The use of fluorides in analysis is , however, undesirable—platinum vessels must be used, and the fluoride ion has to be carefully removed, etc. Tests were carried out on the separation of thorium from solutions containing zirconium, titanium, iron, the rare earths, and some other elements, using the homogeneous precipitation method; these were carried out as follows: to 100 ml of solution containing thorium, zirconium, titanium and the other elements indicated in Table 2 as their chlorides, at a pH of 3 (Congo red paper), was added 1 ml of a 25% solution of calcium chloride and 15 ml of acetonedioxalic acid solution. The solution was boiled for 15 minutes. On the next day the precipitate was filtered through a 9 cm diameter "blue band" filter paper and washed 3-4 times with a 1% solution of oxalic acid. The filter and precipitate were then dried in a 10 ml porcelain crucible, and finally ashed at 600-700°. The residue was transferred to a 50 ml beaker and moistened with



I II

Thorium oxalate crystals obtained by ordinary (I), and homogeneous (II) precipitation.

water, it was then treated while being heated with 3-4 ml of concentrated hydrochloric acid. The acid having been removed so as to leave a damp salt, the residue was dissolved in 8-10 ml of water and transferred to a 25 ml standard flask. The solution was neutralized with ammonia to a pH of 3 (Congo red paper), 2 drops of hydrochloric acid sp.gr. 1.12 was added, and the volume made up to the mark with 0.09 N hydrochloric acid; thorium was finally determined by means of arsenazo [29]. Zirconium trapped by the precipitate of the oxalates of thorium, the rare earths, and calcium was determined by the alizarin method, while titanium was determined by means of hydrogen peroxide [31].

It is clear from Table 1 that thorium can be quantitatively separated from foreign ions by the homogeneous precipitation method. It should be noted that up to 50 γ zirconium and titanium are sometimes coprecipitated, i.e., they are coprecipitated in such amounts as would not interfere (in the presence of tartaric acid) with determination of thorium by means of arsenazo [29].

The rare earths, just like thorium, are precipitated, but they do not interfere in this determination.

A method for the determination of small amounts of thorium in natural materials. 0.5 g of dry sodium peroxide was placed in a 10 ml porcelain crucible and 5-6 mg of ferric oxide added, this was followed by 0.0250 – 0.2500 g of the test ore, and a further 2.5 – 4 g of sodium peroxide. This crucible was placed inside a similar crucible or inside a larger one and placed in a muffle where it was heated until a homogeneous melt (about 550°) was obtained. The cooled melt was dissolved in 60-100 ml of water by heating for 20-25 minutes. After 20 minutes the crucible was withdrawn from the beaker. The solution was filtered through a "white band" filter paper 9-11 cm in diameter, and the hydroxides on the paper washed 2-3 times with 0.5% sodium hydroxide, they were finally dissolved in 20-30 ml of hot 5% (by volume) hydrochloric acid. To this solution a saturated solution of sodium acetate was added until the pH was about 5 (reddening of Congo red paper), water was then added to bring the volume up to 100 ml; 1 ml of a 25% solution of calcium chloride and 15 ml of a

TABLE 2

Separation of Thorium from Foreign Elements

Taken					Found in the precipitate, in γ		
total rare earths, in mg	Zr^{4+} in mg	Ti^{4+} in mg	Fe^{3+} in mg	Th^{4+} in γ	Th^{4+}	Zr^{4+}	Ti^{4+}
10,0	10,0	6,0		38,68	35,0	20,0	—
10,0	10,0	6,0	—	38,68	37,5	—	—
10,0	10,0	6,0	—	38,68	37,5	10,0	—
10,0	10,0	6,0	300,0	38,68	37,5	40,0	5,0
10,0	10,0	6,0	300,0	38,68	35,0	—	—
10,0	10,0	6,0	300,0	38,66	37,5	—	—
10,0	10,0	6,0	300,0	38,63	37,5	—	5,0
10,0	10,0	6,0	300,0	38,68	32,5	50,0	—
0,5	5,5	4,0	60,0	112,0	110,0	50,0	—
0,5	5,5	4,0	60,0	112,0	112,0	10,0	—
0,5	5,5	4,0	60,0	112,0	110,0	—	—

TABLE 3

Determination of Thorium in Natural Materials

Sample number	Major components, in %	Thorium found, in %		Error (relative), in %
		by the fluoride-oxalate-thoron method	by the suggested method	
1	Total rare earths 0,5; TiO_2 6,6; ZrO_2 6,21; Fe_2O_3 62,1; Al_2O_3 11,92	0,12	0,11 0,12	— 2,8
2	Total rare earths 2,27; ZrO_2 7,32; Nb_2O_5 1,19	0,44	0,44 0,43	— 1,0
3	Total rare earths 2,10; ZrO_2 8,24; Nb_2O_5 1,08; Ta_2O_5 0,073	0,16	0,14 0,16 0,16 0,15	— 5,0
4	Total rare earths 0,27; ZrO_2 9,9; Nb_2O_5 0,52; TiO_2 0,027	0,14	0,13 0,14 0,14	0,0
5	Total rare earths 2,24; ZrO_2 6,0; Nb_2O_5 0,47; TiO_2 1,58	0,17	0,15 0,16 0,17 0,17	— 5,0
6	$CaCO_3$	0,002	0,002 0,003	+12,5
7	—	0,005	0,004 0,005	—10,0
8	Total rare earths 2,27; ZrO_2 7,32	0,19	0,22 0,21	+13,0
9	—	0,006	0,005	—20,0
10	ZrO_2 70,0	1,51	1,52	+ 0,7
11	TiO_2 13,42	2,84	2,94	+ 3,6
12	—	0,0016	0,0016	0,00
13	—	0,002	0,002	0,00
14	—	0,040	0,033	—21,0
15	—	0,012	0,012	0,00
16	Total rare earths 0,48; ZrO_2 30,0; TiO_2 1,10; Fe_2O_3 3,80	0,44	0,40	—10,0
17	Total rare earths 0,24; ZrO_2 26,15; TiO_2 0,77; Fe_2O_3 6,60	0,22	0,20	—10,0

acetonedioxalic acid solution were finally added. The solution was boiled for 15-20 minutes and its volume made up to 100 ml again with water, when it was left to stand overnight. On the following day the solution was filtered through a 9 cm "blue band" filter paper. The residue was washed 4-6 times with a 1% solution of oxalic acid. The filter paper and residue were quantitatively transferred to a porcelain crucible in which they were dried and then calcined at 600-700°. This residue was, in turn, quantitatively transferred to a 50 ml beaker and a few drops of water and 4-5 ml of concentrated hydrochloric acid added. The mixture was evaporated until a moist residue was obtained, when another 3-4 ml of concentrated hydrochloric acid was added and the evaporation repeated until a moist residue was obtained again. This moist residue was dissolved in 8-10 ml of water and the solution obtained neutralized with ammonia until the pH was about 3 (Congo red paper); 2 drops of hydrochloric acid sp.gr. 1.12 was added to this solution and the whole transferred to a 25 ml standard flask, 0.5 ml of a 1% ascorbic acid solution was added and the volume made up to the mark with 0.09 N hydrochloric acid.

The solution was shaken up thoroughly and aliquots taken for thorium determination.

2-20 ml of the test solution was transferred to a 25 ml standard flask, and 0.5 ml of a 10% solution of tartaric acid, and 3 ml of a 0.05% solution of arsenazo added, the solution was made up to the mark with 0.09 N hydrochloric acid and thoroughly shaken up. The optical density was measured on a photocolorimeter in 30 mm cells at 570 mμ using a yellow-green filter.

When such a filter is not available it is necessary to combine a green filter with a liquid filter. A saturated solution of potassium dichromate placed in a 10 mm cell in the light path can be used as a liquid filter.

Calculations of the thorium content of the test material are then carried out on the basis of a calibration curve which had been constructed beforehand under the same conditions (from 5 γ to 70 γ of Th in 25 ml of solution).

It is clear from Table 3 that thorium can be determined with reasonable accuracy and reproducibility by the suggested method. Using this method it is possible to determine 0.002 – 3.0% of thorium in ores in the course of 10-12 hours, 10 samples being analyzed in this time.

SUMMARY

1. It has been established that precipitation of thorium from homogeneous solutions by means of acetonedioxalic acid has a number of advantages over the usual oxalate method; a coarse crystalline precipitate which is readily filtered is obtained, while zirconium and titanium are scarcely coprecipitated at all. Thorium can be precipitated quantitatively as the oxalate in the presence of foreign ions; precipitation can be carried out directly without any additional operations.

2. A new method has been developed for the determination of small amounts of thorium (0.002 – 3.0%) in natural materials, in which homogeneous precipitation is used in conjunction with the reagent arsenazo I.

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THE CHROMOMETRIC DETERMINATION OF SEXIVALENT MOLYBDENUM BY MEANS OF TUNGSTEN AND OTHER ELECTRODES•

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A number of papers have been published on the study of the potentiometric titration of sexivalent molybdenum with solutions of divalent chromium salts in media of HCl, H_2SO_4, etc. [1-14]. On the basis of the results obtained, chromometric methods of determining molybdenum in ferromolybdenum, molybdenum concentrates, and other materials have been developed. During titration of molybdenum and accompanying elements, the platinum indicator electrode was used.

On the titration curves obtained in dilute hydrochloric acid there are observed two potential jumps; the first jump—the larger one—corresponds to completion of the reduction of sexivalent molybdenum to the quinquevalent state, while the smaller jump corresponds to the completion of the reduction of the quinquevalent molybdenum to the trivalent state. In concentrated hydrochloric acid, the second jump is greater than the first. All previous investigators have not taken into account the fact that the second jump is located at such low potential values that the platinum electrode may partly function as a hydrogen electrode as a consequence of the acceleration on its surface of the reaction: $2Cr^{2+} + 2H^+ = 2Cr^{3+} + H_2$. This should lead to a decrease in the second potential jump. Accordingly, it is of undoubted theoretical and practical interest to study the titration of sexivalent molybdenum with various electrodes made from materials on which there occurs a high hydrogen overvoltage (metallic mercury, graphite, tungsten, tantalum). It might be expected that such electrodes should permit one to obtain a more clearly defined potential jump for the final reduction of molybdenum to the trivalent state.

EXPERIMENTAL

Reagents, Apparatus and Titration Technique

A solution of sexivalent molybdenum was prepared by dissolving chemically pure ammonium molybdate in water.

This solution was standardized gravimetrically by the lead molybdate method [15]. The values thereby found were: 0.009606; 0.009590; 0.009570 on an average 0.009590 g/ml of Mo.

Solutions of the chloride and sulfate of divalent chromium were prepared and standardized by a method which has been described by one of the authors [16].

All titrations were carried out while a continuous stream of carbon dioxide was passed through the solutions, as is normally done in chromometric methods (without pre-reduction). The solutions being titrated were stirred by means of a mechanical stirrer.

The indicator electrodes used were the normal platinum electrode, a cup-shaped mercury electrode, an amalgamated platinum electrode, a tungsten electrode in the form of a rod (0.3 – 0.4 cm in diameter and 10 cm long) or a tungsten wire, a graphite electrode in the form of a rod (0.5 – 0.6 cm in diameter and 10 cm long),

•From Li Kun's thesis (Moscow State University, 1958).

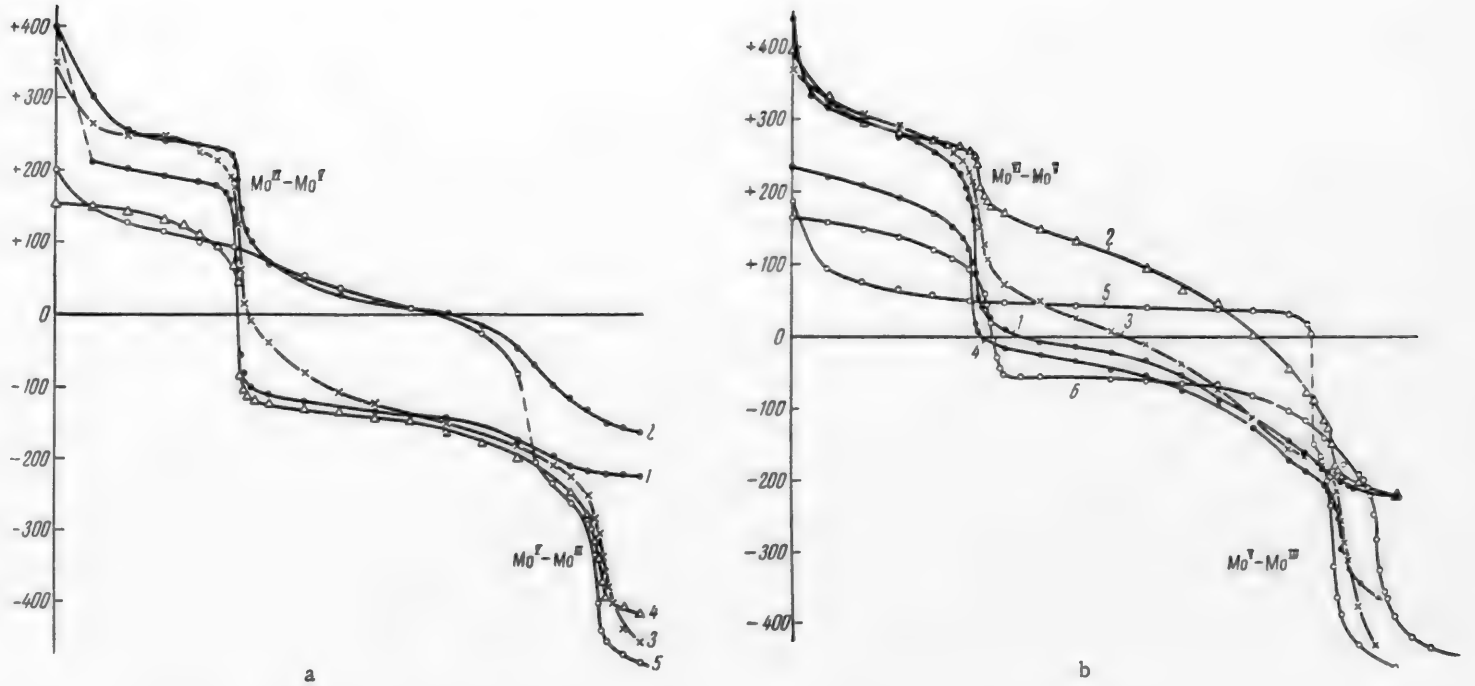

Fig. 1. Titration of sexivalent molybdenum with a divalent chromium salt solution in a sulfuric acid medium using various electrodes: $T_{Cr/Mo^{VI}-V}$ = = 0.009361; temperature 65-75°. Electrodes: 1) platinum; 2) amalgamated platinum; 2) graphite; 4) tungsten; 5) mercury; 6) tantalum.

a) 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) was taken. 70 ml of 10% H_2SO_4 was added. The first potential jump ($Mo^{VI} \rightarrow Mo^{V}$) for the platinum, amalgamated platinum, graphite and tungsten electrodes was observed on adding 5.20 ml of $CrCl_2$ solution. This corresponds to 0.04868 g Mo. The first potential jump was not observed in the case of the mercury electrode. The second potential jump occurred ($Mo^{V} \rightarrow Mo^{III}$) on addition of 15.40 ml of $CrCl_2$ solution (0.04805 g Mo) in the case of the tungsten and graphite electrodes, on addition of 15.30 ml $CrCl_2$ (0.04777 g Mo) in the case of the mercury electrode; no jump was observed in the case of the platinum electrode.

b) 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) was taken. 70 ml of 30% sulfuric acid was added. The first potential jump ($Mo^{VI} \rightarrow Mo^{V}$) for the platinum, amalgamated platinum, graphite, and tungsten electrodes was observed on adding 5.20, 5.30, 5.20, and 5.20 ml respectively of $CrCl_2$ (0.04868, 0.04961, 0.04868, and 0.04961 g of Mo). The mercury electrode did not give a potential jump. The second potential jump ($Mo^{V} \rightarrow Mo^{III}$) occurred for the amalgamated platinum, graphite, tungsten, and mercury electrodes on addition of 15.30, 15.50, 15.50, and 15.30 ml of $CrCl_2$ solution respectively (0.04777, 0.04836, 0.04777 g Mo). The second potential jump was not given by the platinum electrode.

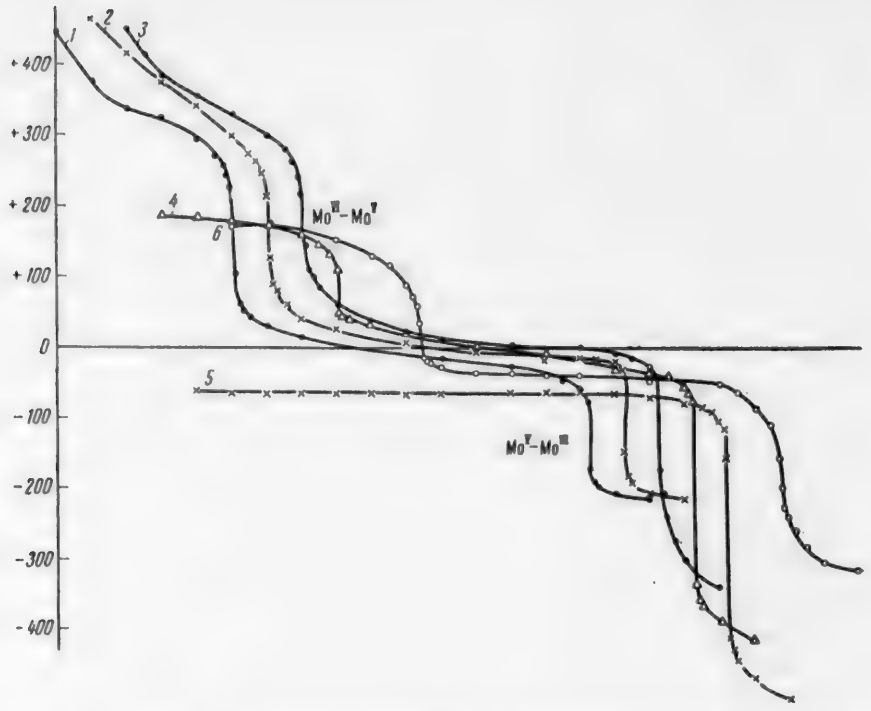

Fig. 2. Titration of sexivalent molybdenum in hydrochloric acid when various indicator electrodes are used.
5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo) was taken; 70 ml of HCl 1:1 was used; temperature 70-75°;

$$T_{Cr/Mo^{VI} \rightarrow V} = 0.009490$$

Electrodes: 1) platinum; 2) amalgamated platinum; 3) graphite; 4) tungsten; 5) mercury; 6) tantalum. The first potential jump ($Mo^{VI} \rightarrow Mo^{V}$) on the platinum, amalgamated platinum, graphite, and tungsten electrodes was found on addition of 5.10 ml of $CrCl_2$ solution (0.04840 g). The first jump was not observed with a mercury electrode. The second jump ($Mo^{V} \rightarrow Mo^{III}$) was found after addition of 15.30 ml of $CrCl_2$ solution (0.04840 g Mo) for all the electrodes studied.

and a tantalum electrode in the form of a plate. The reference electrode was a saturated calomel electrode (all potentials are given with reference to this electrode).

Titration was carried out by a compensation method (P-4 potentiometer) in hydrochloric acid (10 or 30%) at 65-75°, or in a sulfuric acid medium. For each titration 5.0 ml of 0.1 M ammonium molybdate (0.009590 g/liter Mo) was taken together with 70 ml of 10 or 30% hydrochloric acid or 70 ml of 18% sulfuric acid. The beaker used for titration had a capacity of 150 ml. Near the equivalence point the solution of divalent chromium salt was added in 0.10 ml aliquots.

Titration curves obtained in a sulfuric acid medium are shown in Fig. 1a and b, while those obtained in hydrochloric acid are shown in Fig. 2.

DISCUSSION OF RESULTS

It is clear from Fig. 1a and b that the second potential jump obtained during titration of molybdenum in a sulfuric acid medium increases sharply on replacing the platinum electrode by a tungsten and by a graphite electrode, as was to be expected. During titration with a mercury electrode there is observed one large potential jump corresponding to completion of the reduction of molybdenum to the trivalent state. In addition, when

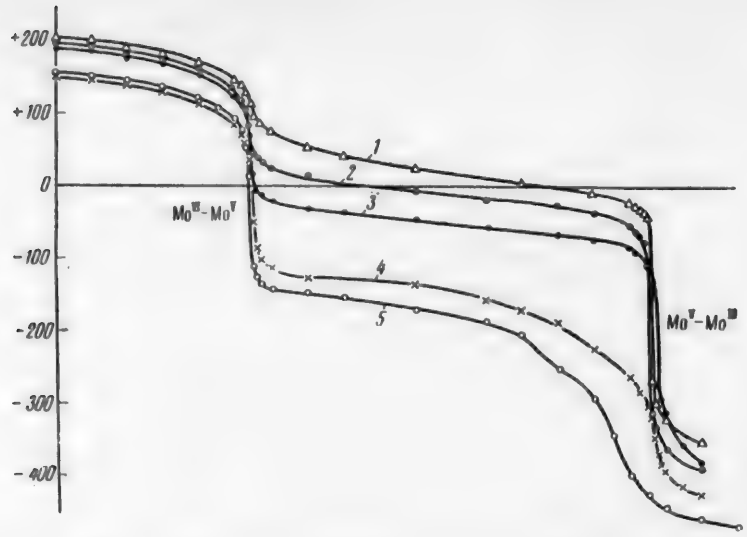

Fig. 3. Effect of sulfuric or hydrochloric acid concentration on the titration curves of sexivalent molybdenum when a tungsten electrode is used. 5.0 ml lots of 0.1 M ammonium molybdate (0.04795 g Mo) taken together with 70 ml of H_2SO_4 or HCl of varying concentrations; temperature 65-70°; $N_{CrCl_2} = 0.09091$; $T_{Cr/Mo} = 0.008723$. Curve 1) 70 ml HCl 2:1; 2) 70 ml HCl 1:1; 3) 70 ml HCl 1:2; 4) 70 ml 10% H_2SO_4; 5) 70 ml 4% H_2SO_4. The first potential jump on curves 1-5 was observed on addition of 5.50 ml of $CrCl_2$ solution (0.04797 g Mo). The second potential jump found on Curves 1 and 2 was on addition of 16.60 ml of $CrCl_2$ (0.04827 g Mo); on Curve 3 the jump was observed after addition of 16.80 ml of $CrCl_2$ solution (0.04885 g Mo); on Curve 4, on addition of 16.70 ml of $CrCl_2$ (0.04856 g Mo); on Curve 5 no potential jump was observed.

a mercury electrode is used, another jump can be observed before the molybdenum changes over into the trivalent state (the dotted line on Curve 5 Fig. 1a and b). The position of this jump changes from titration to titration and is connected with the disappearance of the film formed earlier on the mercury surface. A potential jump corresponding to completion of the reduction of sexivalent to quinquevalent molybdenum is not observed. This can be explained by the fact that mercury in a strongly acid medium reduces a small amount of sexivalent molybdenum to the quinquevalent state with formation of an equivalent amount of univalent mercury ions (formation of a film can be observed on the mercury surface). The reaction proceeds on the electrode surface. During titration with a solution of a divalent chromium salt there occurs reduction of both molybdenum and of the ions of univalent mercury formed (the film on the mercury surface dissolves), accordingly, there is observed a potential jump at the point corresponding to completion of reduction of molybdenum to the trivalent state. Obviously, a mercury indicator electrode can only be used during titration of sexivalent molybdenum in pure solutions, and in the presence of elements which are not reduced by divalent chromium ions. This fact appreciably lowers the practical value of the mercury indicator electrode. As for the amalgamated platinum electrode, this functions approximately like a platinum electrode and not like a mercury electrode. When an amalgamated platinum electrode is used there is observed a comparatively small but quite clearly defined potential jump on completion of the reduction of sexivalent molybdenum to the quinquevalent state, while with a platinum electrode (under equal conditions) there is observed a well defined potential jump. When a platinum electrode and an amalgamated platinum electrode are used respectively, a clearly defined potential jump is not observed at the point corresponding to completion of reduction of quinquevalent molybdenum to the trivalent state under the conditions chosen.* With a tantalum electrode there are observed two clearly defined

*An amalgamated platinum electrode behaves like a platinum electrode not only during titration of sexivalent molybdenum, but also during titration of quadrivalent titanium with a solution of a divalent chromium salt [17].

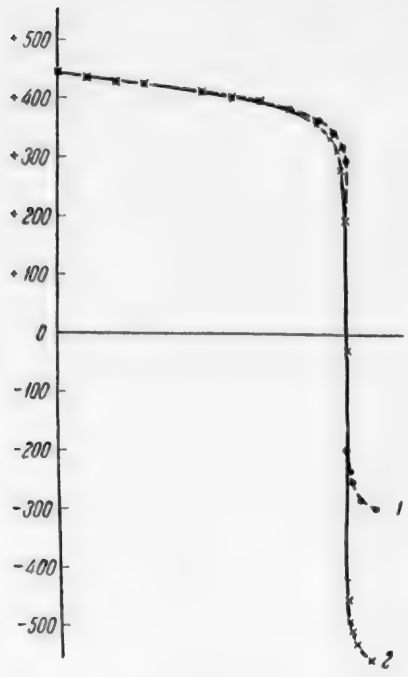

Fig. 4. Titration of trivalent ion with $CrCl_2$ using tungsten and platinum indicator electrodes.
Solutions taken: 10.0 ml 0.1000 N $K_2Cr_2O_7$, 0.6 g Mohr salt, and 40 ml 4% H_2SO_4; room temperature; N_{CrCl_2} = = 0.09980. The equivalence point in both cases was found on addition of 10.2 ml of $CrCl_2$; 1) platinum electrode; 2) tungsten electrode.

potential jumps corresponding to completion of the reudction of sexivalent molybdenum to the quinquevalent state, and completion of the reduction of quinquevalent molybdenum to the trivalent state, in that order. This electrode, however, has no advantages over the tungsten or graphite electrodes for carrying out potentiometric titrations.

It should be noted that during titration of molybdenum in sulfuric acid, the potential of all the electrodes studied, during the transition from Mo^V to Mo^{III} is not established rapidly; accordingly, near the end-point it is necessary to wait for 2-3 minutes after addition of each aliquot of the divalent chromium salt solution.

It is clear from Fig. 2 that during titration of sexivalent molybdenum in a hydrochloric acid medium, when various indicator electrodes were used, in general, the same features are observed as for titration in a sulfuric acid medium. The essential difference is that with a platinum and with an amalgamated platinum electrode in a hydrochloric acid medium there is observed a completely clearly defined second potential jump, while when sulfuric acid is used this second jump is not observed when the electrodes indicated are used. The second potential jump is very distinct when tungsten and graphite electrodes are used, and, when identical conditions are used, this jump is approximately twice the jump obtained with a platinum indicator electrode, and extends into a region of considerably more negative potentials.

The potential of the platinum, amalgamated platinum, graphite, and tantalum electrodes in a medium of HCl 1:1 is established slowly during reduction of Mo^{VI} to Mo^V and of Mo^V to Mo^{III}. The potential of the tungsten and mercury electrodes is established rapidly.

Thus, the tungsten indicator, and also the graphite indicator electrodes have undoubted advantages over the platinum electrode during titration of sexivalent molybdenum in a medium both of sulfuric acid and of hydrochloric acid. The distinct and fairly large potential jump observed at the second equivalence point ensures the accurate establishment of the titration end-point, even for small amounts of molybdenum; this leads to an increase in the reliability and accuracy of molybdenum determination, including molybdenum determinations carried out in the presence of other elements.

The effect of the concentration of hydrochloric or sulfuric acid on the titration curves of sexivalent molybdenum when a tungsten indicator electrode is used, is shown in Fig. 3.

On completion of the reduction of sexivalent molybdenum to the quinquevalent state in a hydrochloric acid medium (2:1, 1:1, and 1:2) there are observed comparatively small, but still quite distinct, potential jumps on the tungsten electrode. The first potential jumps increase with decreasing hydrochloric acid concentration. During titration in a hydrochloric acid medium, the second potential jumps which correspond to completion of reduction of quinquevalent molybdenum to the trivalent state, are considerably larger than the first. The value of the potential jumps increase, in this case, with increasing hydrochloric acid concentration.

Up to the first potential jump, the potential of the tungsten electrode is established rapidly in HCl. Between the first and second jumps, the potential is established rapidly in HCl (2:1) and (1:1), but slowly in HCl (1:2).

When sulfuric acid is used (10 and 4%), large and distinct potential jumps are observed for the tungsten electrode on completion of the reduction of sexivalent molybdenum to the quinquevalent state. With increasing sulfuric acid concentration, the potential jump increases somewhat.

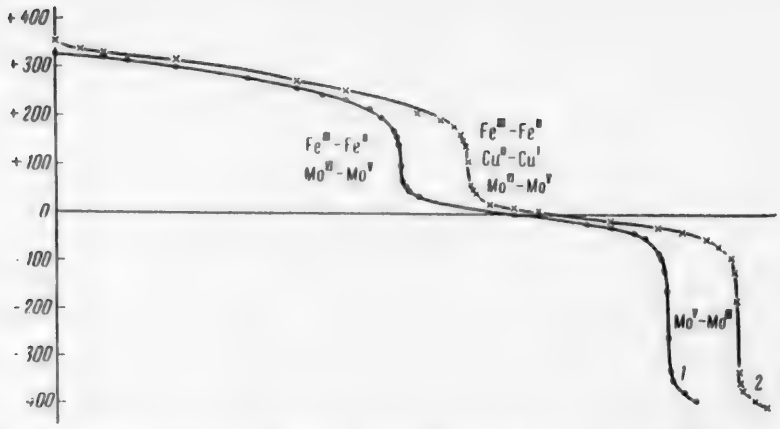

Fig. 5. Titration curves obtained for a solution of sexivalent molybdenum, trivalent iron, and divalent copper in hydrochloric acid, when a tungsten electrode is used. Capacity of titrating cell 250 ml; temperature 65-70°; $N_{CrCl_2} = 0.09090$; $T_{Cr/Mo} = 0.008723$.
Curve 1) 5.0 ml of 0.2 M $NH_4Fe(SO_4)_2$, 5.0 ml 0.1 M ammonium molybdate (0.04795 g Mo) and 70 ml HCl 1:1. The first potential jump was observed on addition of 14.30 ml of $CrCl_2$ solution, while the second jump was observed after addition of 25.40 ml of $CrCl_2$ solution. Curve 2) 5.0 ml of 0.2 M $NH_4Fe(SO_4)_2$, 5.0 ml of 0.1 M ammonium molybdate (0.04795 g Mo), 2.0 ml of 0.1 N $CuSO_4$, 70 ml HCl 2:1. The first potential jump was observed after addition of 17.2 ml of $CrCl_2$ solution, while the second jump was observed after addition of 28.30 ml of $CrCl_2$ solution. In both cases 11.10 ml of $CrCl_2$ (0.04841 g Mo) was used up in reducing quinquevalent molybdenum to the trivalent state.

The potential jump corresponding to reduction of quinquevalent molybdenum to the trivalent state in a medium of 10% sulfuric acid is less distinct than the first jump; it is located at very low potentials, but it is still completely suitable for use in potentiometric titration.

In 4% sulfuric acid the second potential jump is comparatively poorly defined. Molybdenum should be titrated in sulfuric acid by means of the second potential jump only in those cases, where for some reason or other, it is not expedient to work in hydrochloric acid.

On the basis of the results obtained the following conclusions can be drawn. When sulfuric acid is used, molybdenum should be titrated by means of the first potential jump given by a tungsten electrode, while when hydrochloric acid is used with the same indicator electrode, the second potential jump is the best to use, although in this case the first jump could also be used. The dissimilar behavior of molybdenum during titration in sulfuric and hydrochloric acid presumably can be explained by the difference in the state of the molybdenum ions in the sexi-, quinque- and trivalent state in such solutions (in particular, by formation of complex ions). This point will be the subject of a special investigation.

Potentiometric Determination of Molybdenum in Ferromolybdenum Using a Tungsten Electrode

It is necessary to determine molybdenum sometimes in technical materials in the presence of iron and other elements which are also reduced by divalent chromium ions. We accordingly undertook a study of the titration of accompanying elements using a tungsten electrode, and also studied the possibility of titrating molybdenum and other elements in succession.

As is evident from Fig. 4, during titration of iron in a medium of hydrochloric acid with $CrCl_2$ using a tungsten indicator electrode, there is observed a large potential jump at the equivalence point. The potential jump is located on the same place on the titration curve when a tungsten electrode is used as when a platinum

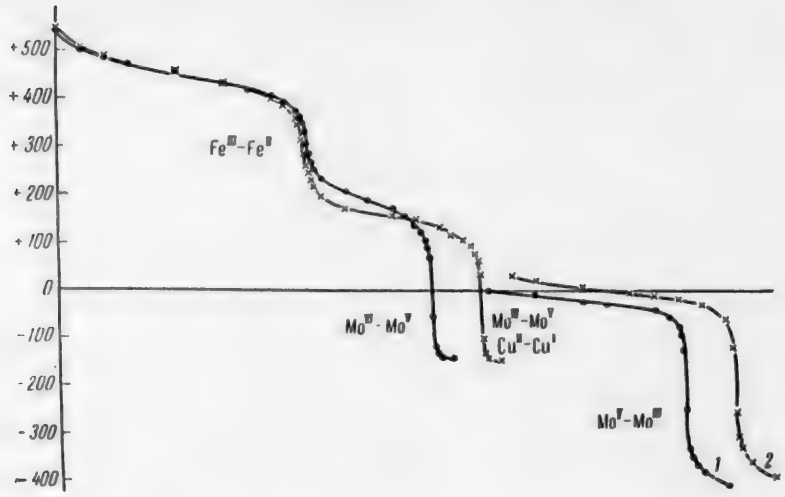

Fig. 6. Separate determination of iron and molybdenum in the absence and in the presence of copper when a tungsten electrode is used. Capacity of titration cell 250 ml; N_{CrCl_2} = 0.09560; $T_{Cr/Mo}$ = 0.009174. Curve 1) 5.0 ml of 0.2 M $(NH_4)_2Fe(SO_4)_2$, 5.0 ml 0.1 M ammonium molybdate (0.04795 g Mo) and 40 ml of 4% H_2SO_4 taken. The first potential jump ($Fe^{III} \rightarrow Fe^{II}$) occurred on addition of 10.40 ml of $CrCl_2$ solution, the second jump ($Mo^{VI} \rightarrow Mo^{V}$) was observed on addition of 15.70 ml of $CrCl_2$. After addition of concentrated hydrochloric acid (100 ml) and titration continued, the third jump ($Mo^{V} \rightarrow Mo^{III}$) was observed after addition of 26.30 ml of $CrCl_2$. 0.04862 g of Mo was found. Curve 2) 5.0 ml of 0.2 M $NH_4Fe(SO_4)_2$, 5.0 ml of 0.1 M molybdate (0.04795 g Mo), 2 ml of 0.1 N $CuSO_4$, and 40 ml of 4% H_2SO_4 were taken. The first potential jump ($Fe^{III} \rightarrow Fe^{II}$) occurred on addition of 10.2 ml of $CrCl_2$, the second jump ($Mo^{VI} \rightarrow Mo^{V}$ and $Cu^{II} \rightarrow Cu^{I}$) was observed after addition of 17.80 ml of $CrCl_2$. After this, 100 ml of concentrated hydrochloric acid was added; the solution was heated to 60-70° and titration continued. The third jump ($Mo^{V} \rightarrow Mo^{III}$) was observed on addition of 28.40 ml of $CrCl_2$. Thus, 10.6 ml of $CrCl_2$ was used up for the reduction of Mo^{V} (Mo found = 0.04862 g).

electrode is used. Thus, the tungsten electrode is fully suitable instead of the platinum indicator electrode for the titration of trivalent iron in dilute sulfuric acid. Near the equivalence point it is necessary to titrate slowly, time being given for the potential to be established after addition of each fresh aliquot of $CrCl_2$ solution. On the titration curve obtained for a mixture of sexivalent molybdenum, trivalent iron, and divalent copper in a hydrochloric acid medium. (2:1), when the tungsten indicator electrode is used (Fig. 5), the first potential jump, which is small but quite distinct, is observed on completion of the simultaneous reduction of the elements indicated to the quinquevalent, divalent, and univalent states respectively; the second, very large jump, corresponds to the completion of the reduction of quinquevalent molybdenum to the trivalent state. Subsequently, univalent copper is reduced to the metal. The amount of chromous chloride used between the first and second potential jumps corresponds to the amount of molybdenum present. Completely satisfactory results have been obtained for molybdenum. Thus, by using a hydrochloric acid medium, it is possible to determine molybdenum in the presence of trivalent iron and divalent copper by means of a tungsten indicator electrode. The amounts of iron and copper, however, cannot be determined at the same time.

Separate determination of iron and molybdenum in the presence, and in the absence of copper is possible under the following conditions (using a tungsten indicator electrode) (Fig. 6). Titration is carried out initially in a CO_2 atmosphere in 4.0% sulfuric acid (40 ml) at room temperature. Under such conditions trivalent iron is first reduced; when this stage is complete there is observed a small but quite distinct potential jump. After this,

Determination of Molybdenum in Ferromolybdenum
(Standard Sample No. 168)
(Specified content, 57.01% Mo)

Expt. No.	Mo found, in %	
1	57.07	57.48
2	56.94	57.07
3	57.12	56.98
4	57.30	57.09

Content of other materials according to specification, in % Cu 0.15; Si 0.55; S 0.23; P 0.032; Cu 0.39; Sn 0.016; Sb 0.018.

divalent copper and sexivalent molybdenum are simultaneously reduced to the univalent and quinquevalent states respectively; when this stage is finished, there is observed a second, large, potential jump. Nevertheless the point at which this second jump occurs is poorly reproduced (over a range of 0.2 – 0.3 ml of 0.1 N $CrCl_2$ solution). The reason for this has not yet been found. After the second potential jump has been reached, 100 ml of concentrated hydrochloric acid (saturated beforehand with CO_2) is added to the solution being titrated, and the whole heated to 60-70°; titration is then continued until a third potential jump is obtained which corresponds to completion of reduction of quinquevalent molybdenum to the trivalent state. The volume of $CrCl_2$ solution expended between the second and third jumps corresponds to the amount of molybdenum present.

When reduction of molybdenum to the trivalent state is complete, reduction of univalent copper to the metal occurs. Satisfactory results have been obtained for iron and molybdenum; the results for copper were poor.

Potentiometric determination of molybdenum in ferromolybdenum is carried out as follows.

One g of finely ground ferromolybdenum is dissolved in a 300 ml beaker in a mixture of 20 ml HNO_3 (1 : 1) and 20 ml H_2SO_4 (1 : 1), and the solution evaporated until the appearance of white fumes of H_2SO_4. After cooling, 70-80 ml of water is added and the mixture heated until the salts dissolve. The cooled solution plus undissolved silica is transferred to a 250 ml standard flask; 100 ml of water is added and the whole shaken thoroughly – this is essential in order to get a homogeneous solution; the volume is then made up to the mark with water. Twenty-five ml of this solution is pipetted into a 250 ml beaker which is to be used for titration, 70 ml of HCl (2 : 1) is then added and the solution heated; CO_2 is passed through the solution to be titrated for 30 minutes, and the solution then titrated slowly with 0.1 N $CrCl_2$ solution at 70°. The indicator electrode used is a tungsten wire. Titration is carried out until a second potential jump is obtained, the chromous chloride used up between the first and second jumps corresponds, as indicated above, to the molybdenum content.

Results obtained by this method are given in the Table.

SUMMARY

A study has been made of the titration of sexivalent molybdenum in hydrochloric and sulfuric acid media, using a divalent chromium salt as titrant, and using various indicator electrodes. A chromometric method has been developed for the determination of molybdenum in ferromolybdenum using a tungsten indicator electrode.

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THE COPRECIPITATION OF ZINC WITH COMPLEX COMPOUNDS CONTAINING PYRIDINE

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The capacity of zinc to be coprecipitated with precipitates of $[MePy_2]X_2$ (where Me is Cu^{2+}, Cd^{2+}, Ni^{2+} and X is SCN^- or Br^-) has already been noted; at that time we very briefly indicated that there is a direct relation between the amounts of the macro- and micro components in solution before precipitation, and the amount of precipitated microcomponent [1]. Such a relation was found in the case of the coprecipitation of cadmium during precipitation of mercury with antipyrine and bromide [2]. We have studied this relation further together with other questions in more detail. Results of these studies are described in the present article.

We shall first of all deal with copreipitation of zinc with $[CuPy_2](SCN)_2$.

Experiments were carried out as follows. In the first series of experiments 1 ml of a 1% solution of ammonium thiocyanate and 0.5 ml of a 10% solution of pyridine were added to 1.5 ml of a solution which was 0.25 N nitric acid, and contained 50 γ of Zn^{2+} and variable amounts of Cu^{2+}. Preliminary tests showed that zinc, when taken separately, does not form a precipitate under the conditions used, but can be precipitated as a result of coprecipitation. The precipitate of $[CuPy_2](SCN)_2$ was washed with a 1% solution of pyridine, and then dissolved in the least possible volume of 1 N nitric acid, and finally titrated from a microburet with 0.1 N silver nitrate in the presence of ferric alum. On the basis of these results the weight of the precipitate was calculated. One ml of 0.1 N silver nitrate corresponds to 16.9 mg of $[CuPy_2](SCN)_2$. After addition of ammonia to the solution obtained, the amount of coprecipitated zinc was determined radiometrically. For this purpose some of the radioactive isotope Zn^{65} was added to the solution used for the work. The specific activity was within the limits of 60-80 impulses/minute per γ of zinc.

The second series of experiments was carried out under the same conditions, but, in this case, the amount of copper was kept constant, while the amount of zinc was altered. 3-5 experiments were carried out in parallel for the given amount of components; usually, they gave almost identical results. On the basis of the results obtained the amount of zinc in 1 mg of the precipitate was calculated, as well as the ratio of the amounts of copper and zinc in the precipitate. When these calculations were made, it was borne in mind that 1 mg of $[CuPy_2](SCN)_2$ contained 189 γ copper.

From the results of the two series of experiments which were carried out at 15-17° (Table 1), it is clear that, if, before precipitation, the amount of copper in solution was, for example, 10 times the amount of zinc, then the amount of copper in the precipitate obtained from this solution was 85 times the amount of zinc. Thus, the relative zinc content of the precipitate is 8.6 times less than in the original solution. This ratio was found to be almost constant in all experiments (Table 1) and equal to 6-8. The small variations around these values can be explained by experimental errors.

It also follows from Table 1 that with increasing copper content of the original solution, or with decreasing amounts of zinc, the content of the latter in the precipitate increases in the first case, and decreases in the second. Nevertheless, in both cases, the amount of coprecipitated zinc found in unit weight of precipitate decreases, and this decrease, as is evident from Fig. 1, is a function of the ratio of $Cu^{2+} : Zn^{2+}$ in the solution before precipitation.

TABLE 1

Coprecipitation of Zinc with $[CuPy_2](SCN)_2$

Contents of solution components before precipitation, in γ		Weight of precipitate, in g		Zinc coprecipitated		Ratio in parts by weight of:	
Zn^{2+}	Cu^{2+}	calc.	found	in γ	in γ/mg of precipitate	in solu. before precip.	in the precipitate
50	500	2,7	2,9	6,3	2,2	10	86
50	750	4,0	4,3	6,5	1,5	15	126
50	1000	5,3	5,8	6,6	1,1	20	172
50	1500	8,0	8,4	6,7	0,8	30	236
50	2000	10,6	10,9	7,0	0,6	40	315
40	1000	5,3	5,8	5,2	0,9	25	210
30	1000	5,3	5,6	4,2	0,7	33	270
20	1000	5,3	5,8	3,2	0,55	50	343
10	1000	5,3	5,4	1,9	0,33	100	572

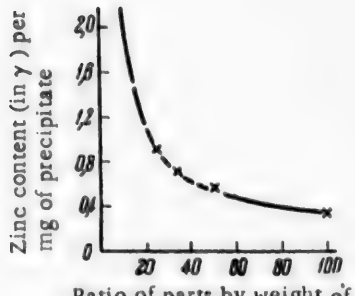

Fig. 1. Zinc content of the precipitate of $[CuPy_2](SCN)_2$ as a function of the ratio in parts by weight of copper and zinc in the solution before precipitation.

—) Experiments carried out with a constant amount of zinc; x) experiments carried out with a constant amount of copper.

The results obtained during the first and second series of experiments lie quite well on one curve. This relation is even more clearly demonstrated in Fig. 2 (Curve 3). The linear nature of this relationship makes it possible to forecast the extent of coprecipitation of zinc under the conditions indicated for the precipitation of $[CuPy_2](SCN)_2$, as long as the contents of the components in the original solution are known.

Similar characteristics were observed during the coprecipitation of zinc with $[CdPy_2](SCN)_2$ and $[NiPy]_2(SCN)_2$.

For precipitating the cadmium compound, 0.25 ml of a 1% solution of ammonium thiocyanate and 0.25 ml of a 10% solution of pyridine were added to 2.5 ml of a solution of a cadmium salt. Since the solubility of $[CdPy_2](SCN)_2$ in water is appreciable, we carried out these tests at 0°. The conditions used for precipitating nickel were the same as those used for copper. Precipitation was carried out at 18-20°. During calculation, it was borne in mind that 1 mg of $[CdPy_2](SCN)_2$ contains 290 γ of cadmium, while 1 mg of $[NiPy_2](SCN)_2$ contains 176 γ of nickel.

The results of these experiments are given in Tables 2 and 3.

In both cases the relative amount of zinc in the precipitate was approximately 1.5 times less than in the original solution. This value was reproduced fairly well in all the experiments; a linear relation was found between the ratio of the amounts of the components in the solution before precipitation, and the amount of coprecipitated zinc contained in unit weight of the precipitate. These results are illustrated in Fig. 2 (Curves 1 and 2).

A series of experiments was carried out on the coprecipitation of zinc with $[CdPy_2]Br_2$.

One ml of a solution containing cadmium and zinc salts was mixed at 18-20° with 0.25 ml of a 50% solution of potassium bromide and 0.25 ml of a 10% pyridine solution. The precipitate formed was washed with 1% pyridine solution, after which it was dissolved in 0.2 ml of 0.1 N nitric acid; the amount of coprecipitated zinc in the solution obtained was determined radiometrically (Table 4). For purposes of calculation it was taken into account that 1 mg of this precipitate contained 263 γ of cadmium.

In the case under consideration, coprecipitation was less, and, consequently, the precipitate contained less zinc than in all the previous cases. Nevertheless, a constant ratio between the components in solution before precipitation and in the precipitate was not observed here; the decrease in the relative amount of zinc in the

TABLE 2

Coprecipitation of Zinc with $[CdPy_2](SCN)_2$

Contents of solution components before precipitation, in γ		Weight of precipitate, in g		Zinc coprecipitated		Ratio in parts by weight of:	
Cd^{2+}	Zn^{2+}	calc.	found	in γ	in γ/mg of precipitate	in solu. before precip.	in the precipitate
300	50	1,03	1,12	34,2	30,5	6	9
500	50	1,72	1,86	34,1	18,3	10	15
750	50	2,52	2,74	33,5	12,2	15	23
1000	50	3,44	3,67	32,8	8,9	20	32
1000	40	3,44	3,67	24,5	6,6	25	44
1000	25	3,44	3,67	14,7	4,0	40	72
1000	12,5	3,44	3,67	6,8	1,8	80	161

TABLE 3

Coprecipitation of Zinc with $[NiPy_2](SCN)_2$ (weight of precipitate 5.7 mg)

Contents of solution components before precipitation, in γ		Zinc coprecipitated		Ratio in parts by wt. of: Ni^{2+} : Zn^{2+}	
Ni^{2+}	Zn^{2+}	in γ	in γ/mg of precipitate	in solu. before precip.	in the precipitate
1000	50	36,0	6,3	20	27
1000	40	27,6	4,8	25	36
1000	30	20,7	3,6	33	48
1000	20	13,8	2,3	50	76
1000	10	6,9	1,2	100	100

TABLE 4

Coprecipitation of Zinc with $[CdPy_2]Br_2$

Contents of solution components before precipitation, in γ		Weight of precipitate, in g		Zinc coprecipitated		Ratio in parts by weight of:	
Cd^{2+}	Zn^{2+}	calc.	found	in γ	in γ/mg of precipitate	in solu. before precip.	in the precipitate
1000	50	3,8	3,7	0,3	0,081	20	3209
1500	50	5,7	5,6	0,4	0,071	30	3662
2000	50	7,6	7,3	0,4	0,055	40	4727
2500	50	9,5	9,2	0,5	0,054	50	4814
5000	50	19,0	18,6	0,6	0,032	100	8109
2000	40	7,6	7,3	0,25	0,034	50	7647
2000	30	7,6	7,3	0,15	0,020	66	13000
2000	20	7,6	7,3	0,1	0,013	100	26000

precipitate varied from 80-200 times. These variations can be explained on the basis of the small extent of coprecipitation, as a result of which the accuracy of determination of coprecipitated zinc is not high. All the same, even in these experiments, there is still observed the same qualitative relationship as in all the reactions noted above (Fig. 2, Curve 4). In all cases there is observed a quite definite relation between the ratio of the

TABLE 5

Coprecipitation of Zinc with $[CuPy_2](SCN)_2$ as a Function of the Temperature (1000 γ Cu^{2+} and 50 γ Zn^{2+}; theoretical weight of precipitate 5.3 mg)

Temp. in °C	Wt. of precipitate, mg	Zinc coprecipitated in γ	Zinc coprecipitated in γ/mg of precipitate
0	5,2	7,8	1,5
10	5,2	7,0	1,3
20	5,2	6,0	1,1
30	5,2	3,5	0,7
40	5,1	2,8	0,55
60	5,2	2,0	0,4
80	5,1	1,0	0,2
100	5,1	0,4	0,08

TABLE 6

Coprecipitation of Zinc with $[CuPy_2](SCN)_2$ at 100° as a Function of the Amount of Zinc in Solution (1000 γ Cu^{2+}; theoretical weight of precipitate 5.3 mg)

Zinc content, in γ	Wt. of precipitate, mg	Zinc coprecipitated in γ	Zinc coprecipitated in γ/mg of precipitate
100	5,1	0,48	0,09
150	5,1	0,84	0,16
200	5,1	1,90	0,37
500	5,3	101,0	19,0
750	5,6	254,0	45,3
1000	6,0	462,0	77,0

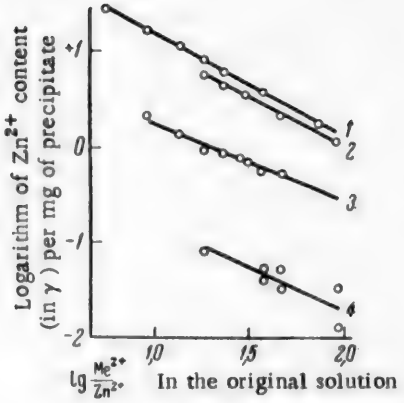

Fig. 2. Relationship between the ratio of the amounts of the components in the solution before precipitation, and the zinc content of 1 mg of precipitate (on a logarithmic scale):
1) precipitation of $[CdPy_2](SCN)_2$;
2) precipitation of $[NiPy_2](SCN)_2$;
3) precipitation of $[CuPy_2](SCN)_2$;
4) precipitation of $[CdPy_2]Br_2$.

amounts of the components in the original solution, and in the precipitate obtained from this solution. (Fig. 2). A significant fact is that all the lines in Fig. 2 are almost parallel to each other. This indicates the general nature of the relationship observed (at least in the case of the reactions studied). That such relationships are possible, can probably be attributed to the fact that in each series of experiments, when the temperature is kept constant, the relative amount of coprecipitated zinc (as a percentage) is almost a constant.

Experiments showed that the extent of the coprecipitation of zinc with $[CuPy_2](SCN)_2$ and $[CdPy_2]Br_2$ is small. By using these reactions it is possible to carry out a fairly satisfactory separation of zinc from copper or cadmium. Microdetermination of the last two cations as the complex compounds indicated gives completely satisfactory results, since the weight of precipitate determined experimentally coincides with the theoretical value within the limits of experimental error (Tables 1 and 4). Separation of copper and zinc can be carried out with even greater completeness, by precipitating $[CuPy_2](SCN)_2$ at an elevated temperature (Tables 5 and 6).

On increasing the temperature of a solution containing 1000 γ Cu^{2+} and 50 γ Zn^{2+} to 100°, the weight of precipitate obtained hardly changes at all, but the amount of zinc which is coprecipitated decreases sharply. On increasing the amount of zinc in the solution while the copper content is kept constant, the weight of the precipitate gradually increases, and the quantity of zinc coprecipitated also increases.

It is of interest to note that in an experiment in which 500 γ of Zn^{2+} was used, the theoretical amount of precipitate was obtained, this apparent high accuracy is, of course, the result of mutual compensation of counteracting sources of error; incomplete precipitation of copper is compensated by coprecipitation of zinc. These results show that 200 γ of Zn^{2+} can be satisfactorily separated from 1000 γ copper, and that quantitative microdetermination of copper by precipitation of the compounds indicated [3] gives satisfactory results, even when small amounts of zinc are present in the solution. Furthermore, the results indicated above for the theoretical weight of precipitate, and that found by titration, show that a titrimetric method is fully applicable

TABLE 7

Titrimetric Microdetermination of Copper in the Presence of Zinc

Content in γ of:		0.1 N $AgNO_3$ used, in ml	Cu^{2+} found, in γ	Error	
Cu^{2+}	Zn^{2+}			in γ	in %
1000	50*	0,30	953	47	4,7
1000	100*	0,30	953	47	4,7
1000	150*	0,30	953	47	4,7
1000	200*	0,30	953	47	4,7
1000	500*	0,32	1017	17	1,7
1000	750*	0,33	1048	48	4,8
1000	1000*	0,35	1112	112	11,2
1000	10**	0,32	1017	17	1,7
1000	20**	0,34	1080	80	8,0
1000	30**	0,33	1048	48	4,8
1000	40**	0,34	1080	80	8,0
1000	50**	0,34	1080	80	8,0

*Precipitation at 100°.

**Precipitation at 20°.

to the determination of copper in the form of $[CuPy_2](SCN)_2$. Naturally, a titrimetric microdetermination can be carried out appreciably more rapidly and simply than a gravimetric determination. Table 7 contains results obtained during the titrimetric microdetermination of copper in the presence of zinc. Precipitation of $[CuPy_2](SCN)_2$ was carried out at room temperature and at 100° from 3 ml of a nitric acid solution. Precipitation conditions, as well as washing and titrating were the same as those described above.

SUMMARY

It has been found that during the coprecipitation of zinc with $[MePy_2](SCN)_2$ there exists a definite relationship between the amounts of the components in solution before precipitation and in the precipitate formed.

The amount of zinc which is coprecipitated decreases sharply with increasing temperature; this makes it possible to separate copper from zinc, and to determine copper quantitatively in solution.

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A STUDY OF THE REACTION OF CUPRIC IONS WITH POTASSIUM THIOCYANATE

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It is known that black cupric thiocyanate $Cu(SCN)_2$ is gradually reduced to CuSCN in aqueous media [1]. When the solution is diluted with water CuSCN is deposited in the form of a white precipitate. Philip and Bramley [1] were of the opinion that in acetone solution the reduction proceeds considerably more slowly than in water. Reduction occurs readily in the presence of any reducing agent, for example sulfurous acid. A number of research workers have used this reaction for the quantitative determination of copper [2-5]. Kul'berg and Gorlinskii [6] have studied the interaction of cupric ions with potassium thiocyanate taken in excess, by means of a spectrophotometric method in aqueous acetone solution; they concluded that the reason for the color is the formation of cuprothiocyanate ions $[Cu(SCN)_n]^{n-2}$, where n is 3 or 4. Later, Kitson [7], and Oudinet and Gallais [8], carried out some work with the aim of establishing an accurate formula for cuprothiocyanate complexes, and for determining the stability of these complexes in 50% and 70% acetone-water mixtures; they carried out this work on an electrophotometer. These authors, using Job's method [9], determined the composition and instability constants of the thiocyanate complexes of divalent copper in aqueous acetone solutions; they found that, depending on the concentration of the alkali metal thiocyanate, several complexes can exist at the same time: $[Cu(SCN)_3]^-$, $[Cu(SCN)_4]^{2-}$, $[Cu(SCN)_5]^{3-}$; of these, the one which predominates according to the authors is the complex with an instability constant of $6.5 \cdot 10^{-6}$ at 18°.

Kitson [7] has suggested a spectrophotometric method of determining copper, cobalt, and iron in each others presence by means of ammonium thiocyanate in 50% aqueous acetone solution, to which potassium periodate is added for preventing reduction of Cu^{II}.

Thus the thiocyanate complexes of Cu^{II} have been studied, and also used for the quantitative determination of copper in aqueous acetone solution only. Accordingly, we thought it would be interesting, both from a practical and a theoretical point of view, to study the reaction of Cu^{II} ions with potassium thiocyanate in aqueous solution.

For preventing reduction of Cu^{II} ions, dilute solutions of hydrogen peroxide, ammonium or sodium persulfate, and nitric acid were used as oxidizing agents. The most suitable oxidizing agent for this purpose proved to be dilute nitric acid (pH about 3), which does not react with thiocyanate ions to form colored compounds.

Meta- and ortho-phosphoric acid were used as complexing agents for preventing reduction of Cu^{II} ions by thiocyanate ions in aqueous solution. In the presence of Cu^{II} and thiocyanate ions there is formed a stable compound with a yellow-green color. Apparently, this compound is a thiocyanate-phosphate complex.

The following materials were used: 1) freshly crystallized cupric sulfate; 2) potassium thiocyanate, chemically pure grade; 3) nitric acid (1 : 1); 4) zinc sulfate, chemically pure grade; 5) ferric sulfate, chemically pure grade; 6) aluminum sulfate, chemically pure grade; 7) metaphosphoric acid (saturated aqueous solution).

The copper content of the solution was determined iodometrically. The optical density of the solutions was measured on FEK-M and FNK-51 (blue filter) photoelectric colorimeters.

Interaction of Cupric Ions with Potassium Thiocyanate in the Presence of Nitric Acid

For establishing the effect of the amount of KSCN on its interaction with Cu^{II}, equal amounts of cupric sulfate and nitric acid, and various amounts of potassium thiocyanate (from 1 to 15 ml) were introduced into

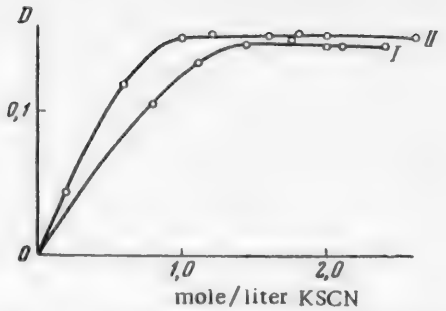

Fig. 1. The relation between the optical density of solutions of the copper thiocyanate complex, and the amount of potassium thiocyanate in the presence of nitric acid and metaphosphoric acid. Cupric sulfate concentration $1.2 \cdot 10^{-4}$ mole/liter Total volume of solution 25 ml: I) 0.2 ml of nitric acid (1 : 1) added; II) 1.0 ml of a saturated solution of metaphosphoric acid added.

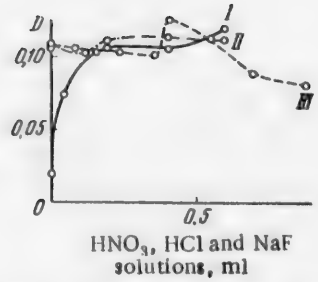

Fig. 2. The effect of HNO_3, HCl, and NaF on the optical density of the thiocyanate complex of divalent copper. Cupric sulfate concentration $1.6 \cdot 10^{-4}$ mole/liter, concentration of potassium thiocyanate 2.0 mole/liter. Total volume of solution 25 ml: I) HNO_3 (1 : 1) added; II) HCl (1 : 1) added; III) 1 N NaF added.

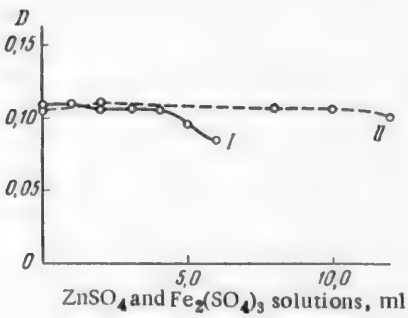

Fig. 3. Effect of zinc and iron ions on the optical density of solutions of the copper thiocyanate complex. Cupric sulfate concentration $1.6 \cdot 10^{-4}$ mole/liter; potassium thiocyanate concentration 2.0 mole/liter; 0.2 ml of nitric acid (1 : 1) was added. Total volume of solution 25 ml: I) $1.0 \cdot 10^{-5}$ mole/liter of $Fe(SO_4)_3$ added; II) 2.0 N $ZnSO_4$ solution added.

25 ml standard flasks. The solutions were made up to mark with water and then shaken; after 15 minutes their optical density was measured. As is evident from Fig. 1, with increasing potassium thiocyanate concentration, the optical density of the solutions increases up to a certain value and then remains constant.*

The effect of the amount of nitric acid for constant concentrations of Cu^{II} and potassium thiocyanate and the effect of hydrochloric acid on the optical density is illustrated in Fig. 2.

Addition of even small amounts of nitric acid sharply increases the optical density of the solution as compared with that of solutions to which no nitric acid has been added. Nevertheless, addition of more than 0.6 ml of nitric acid per 25 ml of solution increases the optical density of the solution even in the absence of copper; this can probably be explained by the formation of colored products by the interaction of nitric acid and potassium thiocyanate. Variations in amount of hydrochloric acid from 0.12 to 0.5 ml have almost no effect on the optical density. The presence of hydrochloric acid presumably does not affect the composition of the copper thiocyanate complex.

During a study of the effect of Zn^{2+} ions on the color of the copper thiocyanate complex, the zinc concentration was more than 100 times that of the copper concentration, as Fig. 3 shows (Curve 1); zinc ions do not interfere with the formation of the copper thiocyanate complex.

Over the concentration range studied in the case of iron ($4 \cdot 10^{-7}$ – $2.5 \cdot 10^{-6}$ g/ml), interference from iron was successfully suppressed by means of 2 N sodium fluoride solution (Fig. 3).

*Very dilute potassium thiocyanate solutions do not give a color.

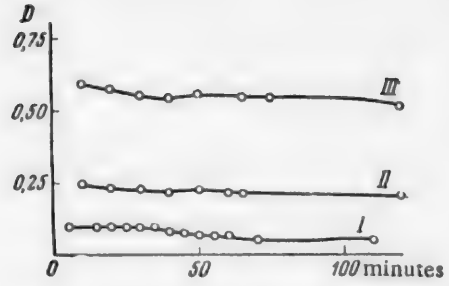

Fig. 4. Stability with time of the thiocyanate and phosphate-thiocyanate complexes of divalent copper. Total volume of solution, 25 ml.
I) Copper concentration $1.6 \cdot 10^{-4}$ mole/liter, potassium thiocyanate concentration $1.2 \cdot 10^{-4}$ mole/liter; 0.3 ml of 1 N sodium fluoride and 0.2 ml of nitric acid (1 : 1) added; II) copper concentration $1.6 \cdot 10^{-4}$ mole/liter, potassium thiocyanate concentration 1.2 mole/liter; 1 ml of a saturated solution of metaphosphoric acid added; III) copper concentration $4.0 \cdot 10^{-4}$ mole/liter, potassium thiocyanate concentration 2 moles/liter; 1 ml of a saturated solution of metaphosphoric acid added.

Results of measurements of the optical density of solutions of the cupric thiocyanate complex carried out at various sodium fluoride concentrations, show that the addition of large amounts of sodium fluoride lowers the color intensity of the solution; nevertheless, over a fairly extensive concentration range of the fluoride (0–0.5 ml of 1 N fluoride per 25 ml solution) the optical density of the solution is almost constant (Fig. 2, Curve III).

As Fig. 4 shows, the optical density of a solution of the thiocyanate complex of copper does not change in the course of 35 minutes.

As Fig. 5 shows, at concentrations of $5 \cdot 10^{-3} - 2.8 \cdot 10^{-2}$ g of Cu/liter, solutions of the complexes, in the presence of excess potassium thiocyanate, conform to the Beer law.

For low copper concentrations, this reaction is suitable for the photometric determination of copper in weakly nitric and hydrochloric solutions, in the presence of large amounts of zinc and small amounts of iron.

Interaction of Divalent Copper with Potassium Thiocyanate in the Presence of Metaphosphoric Acid

It was noted that the stability of the thiocyanate complex of Cu^{II} increases in the presence of metaphosphoric acid. Solutions of $CuSO_4$ containing metaphosphoric acid and potassium thiocyanate preserve their yellow-green color over a prolonged period. In the absence of metaphosphoric acid the color disappears rapidly, the solution gradually becomes turbid (when sufficient copper is present) while metaphosphoric acid prevents decolorization even in the presence of a reducing agent.

As the potassium thiocyanate concentration increases, the initial optical density of the solutions increases (Fig. 1), but, the higher the KSCN concentration, the greater the drop in optical density in the first minutes after mixing the solutions. It was observed, however, that after 15-20 minutes, the optical density assumes an equal value over a fairly wide potassium thiocyanate concentration range (Fig. 1).

Color stability is sufficient (Fig. 4) for using it for photometric measurements.

For copper concentrations of $2.5 \cdot 10^{-3} - 3.5 \cdot 10^{-2}$ g/liter the solutions obey Beer's law satisfactorily.

The color develops in moderately acid solution. At a pH of less than 1.8 the solution becomes turbid, while at a pH greater than 4 the solutions become decolorized. Maximum color intensity is achieved at a pH of 2-3. Substitution of meta- by orthophosphoric acid did not lead to any improvement. Potassium thiocyanate cannot be replaced by ammonium thiocyanate (because of the effect of ammonium ions).

The potassium thiocyanate must be added to the $CuSO_4$ solution after the addition of metaphosphoric acid. When KSCN is added to the $CuSO_4$ solution before metaphosphoric acid, rapid reduction of Cu^{II} to Cu^{I} with formation of a precipitate occurs; metaphosphoric acid, presumably, complexes Cu^{II} and thereby prevents its reduction. This is indirect proof of the fact that potassium thiocyanate does not react simply with the cupric ions, but with complex phosphate ions of Cu^{II}.

Chloride ions do not affect the color intensity at concentrations up to 0.15 g/ml, for a copper concentration of about 10^{-5} g/liter, i.e., at a limiting ratio of 15,000 : 1. At higher chloride concentrations, the optical density increases somewhat.

Aluminum does not affect the color intensity (solutions containing 250 times more aluminum than copper were tested); neither does zinc interfere.

The color of solutions of ferric thiocyanate does not disappear on addition of metaphosphoric acid to them, but only changes to a yellow-green, which is similar to the color of the phosphate-thiocyanate complex of divalent copper. Decolorization only occurs on raising the pH to 5, but, this, as indicated above, also leads to decolorization of the phosphate-thiocyanate complex of copper. Iron should not be present in solution in amounts which are twice that of the copper.

The results obtained show that the colored phosphate-thiocyanate complex of copper can be used for the photometric determination of copper in solutions containing large amounts of aluminum and zinc, and small amounts of iron. The sensitivity of the reaction is $2.5 \cdot 10^{-6} - 3.5 \cdot 10^{-5}$ g/ml.

Thus, determination of copper can be carried out both by means of its thiocyanate and phosphate-thiocyanate complexes. In both cases calibration curves are constructed within the coordinates: copper concentration – optical density. The latter is measured on a photocolorimeter provided with a blue filter.

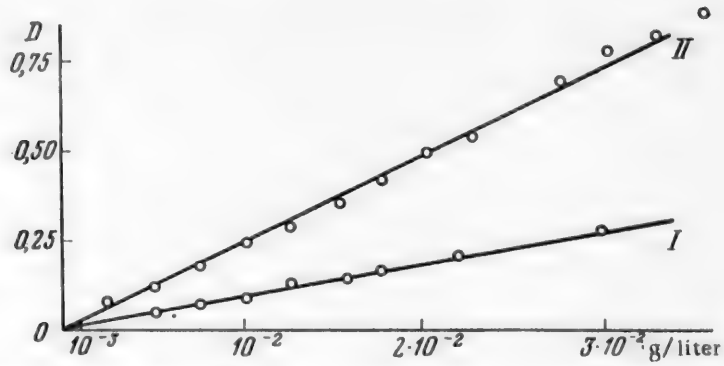

Fig. 5. Relation between the optical density of solutions of the thiocyanate and the phosphate-thiocyanate complexes of copper, and copper concentration (conformity to the Beer law).
I) Copper thiocyanate complex; II) copper phosphate-thiocyanate complex.

Standard solutions to be used for the first method are prepared by introducing from 1 to 5 ml of a $CuSO_4$ solution of known concentration (of the order of 10^{-4} mole/liter) into 25 standard flasks, 0.2 ml of HNO_3 (1 : 1) is then added, followed by 8 ml of 4 N KSCN, and 0.3 ml of 1 N NaF; the volume is made up to the mark with water, the flask shaken, and the optical density measured after 15 minutes.

The test solution is treated in the same way.

For the photometric determination of copper by the second variant involving metaphosphoric acid, the same procedure as that outlined above is followed, the sole difference in this case being the addition of 1 ml of saturated metaphosphoric acid instead of sodium fluoride, while the nitric acid is omitted.

SUMMARY

The reaction of cupric ions with potassium thiocyanate in aqueous solution has been studied.

Conditions have been established which guarantee the stability and high color intensity of the copper thiocyanate complex.

It has been shown that it is possible to use potassium thiocyanate for the photometric determination of copper in the presence of nitric and metaphosphoric acids. The reaction is more sensitive than that with ammonia and potassium ferrocyanide.

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THE ELECTROCHEMICAL BEHAVIOR OF AN ALUMINUM ELECTRODE DURING TITRATION OF ALUMINUM IONS WITH FLUORIDE

B. N. Kabanov and L. Ia. Poliak

During the potentiometric titration of aluminum ions by means of a sodium fluoride solution, using the classical method of Treadwell and Bernasconi [1], a small amount of a mixture of Fe^{3+} and Fe^{2+} ions is added in order to set up an oxidation–reduction system. Since the complex $[AlF_6]^{3-}$ is considerably more stable than the complex $[FeF_6]^{3-}$, then, in the course of titration, as long as there are aluminum ions in solution, sodium fluoride will be used up in forming a complex with aluminum. At the end point when all the aluminum ions have been complexed, formation of complex iron compounds starts, and, as a result of this, the potential of the platinum electrode is sharply displaced.

In 1948 an article by Chirkov appeared [2]; in the course of the work described there a successful attempt was made to use an aluminum electrode coupled with a nichrome electrode for the titration of aluminum with sodium fluoride. It is recommended that potentiometric titration of aluminum with sodium fluoride be carried out in a hydrochloric acid media, buffered at a pH of ~5 with sodium acetate, in the presence of sodium chloride.

This method has been used by Budanova and Volodarskaia [3] for the determination of aluminum in bronzes and brasses, and by Gorelova and Poliak [4] for the determination of aluminum in heat-resisting alloys based on nickel.

In all the papers indicated, only practical recommendations are given for the use of an aluminum-nichrome couple for the potentiometric determination of aluminum in various materials. Such questions as the mechanism of the operation of the electrode pair Al – NiCr, the reason for the potential jump at the end point when excess fluoride ions are present in solution, and the effect of cations and anions present in solution on the electrochemical behavior of the electrodes, are not discussed in the papers by S. K. Chirkov and the workers who followed him.

The purpose of the work discussed here was to study the electrochemical behavior of the aluminum electrode under conditions similar to those used during potentiometric titration.

EXPERIMENTAL

1. Potentiometric titration. The first point to settle was which of these two electrodes is the indicator electrode. For this purpose we carried out a compensation titration of an aluminum salt with the pairs NiCr – calomel electrode and Al – calomel electrode as in [4]. These experiments showed that the potential of the nichrome electrode remains constant during titration (Fig. 1, Curve 2), while the potential of the aluminum electrode changes sharply with changes in concentration of the F^- ions (Fig. 1, Curve 2). Thus, potential changes during titration, and the magnitude of the potential jump at the end-point, are determined by changes in the potential of the aluminum electrode only.

In order to clarify the mechanism of the aluminum electrode during potentiometric titration, the following questions must be resolved:

1) by what processes is the stationary potential of the aluminum determined in the given solutions;

2) the effect of accompanying anions (F^-, Cl^-, SO_4^{2-}, CH_3COO^-);

3) the mechanism of the sharp change in the potential of the aluminum electrode at the end-point during compensating and noncompensating potentiometric titration.

2. Polarization measurements. The aluminum electrode is not reversible, its potential is determined neither by the concentration of aluminum ions in solution, nor by the oxidation–reduction potential of the solution, but is usually determined by the relation between two different processes–cathodic and anodic. Such a potential is called stationary.

In order to establish the nature and rates of those anodic and cathodic processes which determine the stationary potential, and the potential of the aluminum electrode when current is flowing during potentiometric titration, polarization curves were taken for the aluminum electrode in pure solutions of sodium fluoride, and in the presence of additions of various salts (acetate, sulfate, and chloride) in various combinations.

The polarization curves on an aluminum electrode were taken by the usual compensation method using a saturated calomel electrode as the reference electrode. The technique used for taking the polarization curves has been described previously [5]. The potential of the polarized aluminum electrode was calculated with respect to the normal hydrogen electrode. Measurements were made at room temperature over the range 10^{-6} – 10^{-3} amp/cm^2 for the density of the polarizing current. Both electrodes (the polarized electrode–aluminum, and the auxiliary electrode–platinum) were placed in a hermetically sealed vessel with ground glass joints. Nitrogen was passed through the solution during the measurements to provide an inert atmosphere. Before each pair of curves (cathodic and anodic) was taken, the electrode was cleaned with glass powder or velvet emery paper, and then with wet and dry filter paper. On immersing the aluminum electrode in the test solution its stationary potential was measured, it was then subjected to polarization by an ever increasing current. Since the stationary potential of the aluminum electrode was not established immediately, the first measurement was made 2-3 minutes after immersion of the electrode in the test solution. The aluminum electrode used was in the form of aluminum wire of high purity (Mark 000) containing 99.999% Al.

Polarization measurements were made under conditions identical to those used for potentiometric titration, i.e., when the polarization curves were taken, the same salt concentration, and the same pH, were used as those adopted for potentiometric titration according to method [4].

In order to establish the effect of the anions Cl^-, CH_3COO^-, and F^-, taken separately and together, on the electrochemical behavior of an aluminum electrode during titration of aluminum, the polarization curves shown in Figs. 2-6* were taken.

DISCUSSION OF RESULTS

The following electrochemical reactions may take place on the surface of an aluminum electrode:

$H^+ + e = \frac{1}{2} H_2$ – discharge of hydrogen ions;
$Al = Al^{3+} + 3e$ – dissolution of aluminum.

Only these two processes occur on an aluminum electrode. When no current passes through the electrode and its potential does not change, then the rate at which hydrogen is evolved and the rate at which the metal will dissolve, will be equal to one another (the stationary state of the system) [6].

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*The concentrations indicated on the figures for the various salts were chosen on the basis of the following considerations.

0.5 N or 0.25 N sodium fluoride solutions are normally used for the potentiometric titration of aluminum. When the volume of solution to be titrated is about 100 ml, and if one assumes that at the end-point the excess sodium fluoride amounts to 0.1 ml, then the concentration of F^- ions at the end-point should be of the order of $\frac{0.1 \cdot 0.5}{100} = 0.5 \cdot 10^{-3}$ M. Accordingly, the concentration of F^- ions in the polarization measurements was 0.001 M.

Titration of aluminum is carried out in the presence of 10 g of NaCl for a total volume of about 80-100 ml. Consequently, the concentration of Cl^- ions in the test solution amounts to $\frac{10 \cdot 1000}{58.5 \cdot 100} \approx 2$ M.

The concentration of CH_3COO^- was calculated in similar fashion.

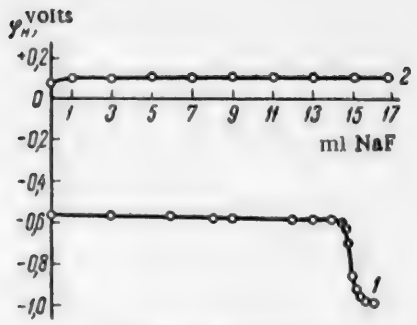

Fig. 1. Curves for the potentiometric titration of aluminum with sodium fluoride:
1) with the electrode pair Al–calomel electrode; 2) with the electrode pair NiCr–calomel electrode.

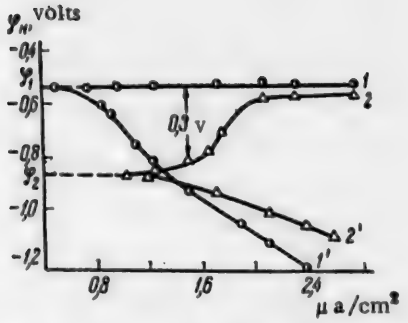

Fig. 2. Polarization curves of the aluminum electrode in the solutions:
1) 2 N NaCl + 1 N CH_3COONa; 2) 0.001 N NaF + 2 N NaCl + 1 N CH_3COONa.

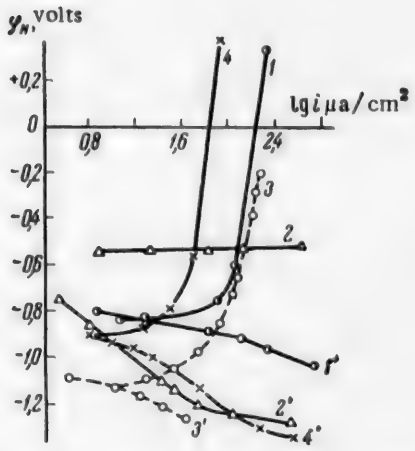

Fig. 3. Polarization curves for an aluminum electrode in solutions of:
1) 0.001 N NaF + 1 N CH_3COONa; 2) 0.001 N NaF + 2 N NaCl; 3) 0.001 N NaF; 4) 0.001 N NaF + N Na_2SO_4.

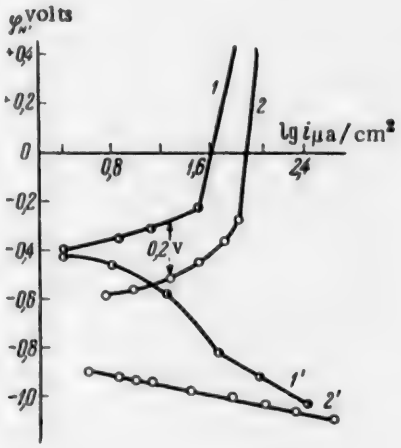

Fig. 4. Polarization curves for an aluminum electrode in solutions of:
1) 0.001 N NaF; 2) 2 N NaCl; 3) 1 N NaF + 1 N Na_2SO_4 + 1 N CH_3COONa.

Dissolution of the metal is shown graphically by the anodic polarization curve, while liberation of hydrogen is shown by the cathodic curve. The point of intersection of the extrapolated cathodic and anodic polarization curves gives the value of the stationary potential of the electrode (Fig. 7).

We measured the stationary potentials of the aluminum electrode during titration in the given solution. The question is, what explains the shift in the stationary potential towards negative values during titration of aluminum with fluoride ions. One of the following cases is possible:

1) the stationary potential is shifted as the result of an acceleration of the anodic process (a decrease in the overvoltage of the process of aluminum dissolution);

2) the stationary potential is shifted as the result of a slowing down of the cathodic process (an increase in hydrogen overvoltage);

3) the stationary potential is shifted as a result of both processes occurring simultaneously.

It is accordingly necessary to establish which of these cases occurs during potentiometric titration of aluminum with sodium fluoride.

Let us analyze the curves obtained.

Polarization curves for the aluminum electrode taken in a mixture of sodium chloride and acetate in the absence of F^- ions and in the presence of the latter (Fig. 2, Curves 1 and 2) show that F^- ions shift the stationary potential of the aluminum electrode towards negative values by 0.3 volt ($\varphi_2 - \varphi_1 = -0.3$ volt).

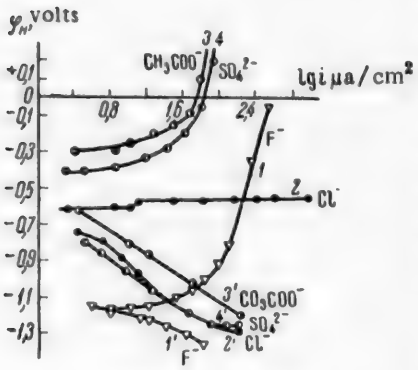

Fig. 5. Polarization curves for an aluminum electrode in solutions of: 1) 0.001 N NaF; 2) N NaCl; 3) 1N CH_3COONa; 4) 1 N Na_2SO_4.

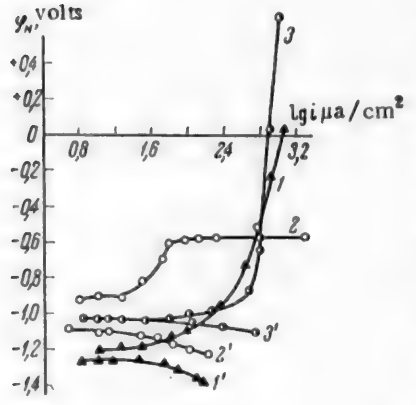

Fig. 6. Polarization curves for an aluminum electrode in solutions of: 1) 0.01 N NaF; 2) 0.01 N NaF + 2N NaCl; 3) 0.01 N NaF + 1 N CH_3COONa.

From a comparison of the titration curve (Fig. 1, Curve 1) and the polarization curve (Fig. 2, Curve 2), it is evident that the values of the potentials of the aluminum electrode during titration and the stationary potentials during polarization measurements are the same, and that, in addition, the potential jump at the end-point is equal in magnitude to the shift in the stationary potential of the aluminum electrode during polarization measurements. For a detailed explanation of the reason for the shift in the stationary potential of the aluminum electrode by 0.3 volt under the influence of F^- ions, it is necessary to consider the effect of each of the anions present on the shape of the cathodic and anodic overvoltage curve.

F^- Ions. a) F^- ions at a concentration of 0.001 N (in the presence of Cl^- and CH_3COO^-) strongly depress the overvoltage of the anodic process of dissolution of the aluminum at low current densities (Fig. 2, Curves 1 and 2) and have almost no effect on the cathodic process (Fig. 2, Curves 1' and 2'). Similar results are obtained for a fluoride concentration of 0.01 N.

Thus, the shift in the stationary potential of the aluminum electrode of 0.3 volt caused by F^- ions at a concentration of 0.001 N, is determined by their accelerating action on the anodic process only—the dissolution of the aluminum.

This activating effect of F^- ions on the aluminum electrode can be explained on the basis of the hypothesis of the adsorptive expulsion of oxygen by fluoride atoms from the electrode surface. The activating adsorption of F^- ions is apparently a slow process, since at comparatively high densities of the anodic current the aluminum, in the absence of chloride ions, is completely passivized (Fig. 3, Curve 1; Fig. 4, Curve 2; and Fig. 5, Curve 1).

b) F^- ions in the presence of SO_4^{2-} and CH_3COO^- ions shift the stationary potential of the aluminum electrode both at the expense of the anodic and cathodic processes (Fig. 4). Thus the mechanism of the shift in the stationary potential caused by F^- ions is different in the presence of Cl^- (Fig. 2) and SO_4^{2-} ions respectively.

c) F^- ions cause the highest hydrogen overvoltage on the aluminum (Fig. 3, Fig. 5, Curves 1', 2', 3', and 4') as compared with the other test ions.

Cl^- Ions. a) In the absence of chloride ions, during anodic polarization of the aluminum electrode, starting at a current density of about 10^{-4} amps/cm², there occurs a sharp shift in the potential toward positive values (complete passivization of the aluminum) (Fig. 3, Curves 1, 3, and 4; Fig. 4, Curves 1 and 2 etc.).

In the presence of Cl^- ions this phenomenon is not observed, Cl^- ions prevent anodic passivization of the aluminum electrode (Fig. 2, Curves 1 and 2; Fig. 3, Curve 2 etc.). The mechanism of the activating effect

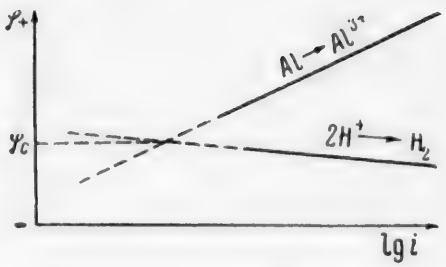

Fig. 7. Establishment of the stationary potential on an aluminum electrode.

of Cl^- ions on iron and magnesium electrodes during anodic polarization has been studied several times [6].

It is worthy of note that the activating effect of chloride ions on aluminum is preserved up to high current densities; this testifies to the high rate of the specific adsorption of the chloride ions.

b) Cl^- ions depress the hydrogen overvoltage in 0.01 N and 0.001 N NaF solution by 0.2 volt (Fig. 3, Curves 2' and 3', and Fig. 6, Curves 1' and 2').

SO_4^{2-} Ions. a) SO_4^{2-} ions at a concentration of 0.1 N also depress the hydrogen overvoltage by 0.2 volt in 0.001 N fluoride solution (Fig. 3, Curves 3' and 4') this could be the result of partial expulsion of F^- from the aluminum surface.

b) SO_4^{2-} ions lower the current density at which the passivized increase in the anodic curve occurs (Fig. 3, Curves 3 and 4), i.e., they decrease the activating effect of the F^- ions.

CH_3COO^- Ions. a) CH_3COO^- ions lower the hydrogen overvoltage on aluminum in 0.001 N NaF by 0.3-0.35 volt (Fig. 3, Curves 1' and 3'; Fig. 6, Curves 1' and 3'), obviously, as a result of high specific adsorption on aluminum.

b) CH_3COO^- ions in the presence of SO_4^{2-} ions, at low current densities, give the lowest hydrogen overvoltage (Fig. 4, Curve 1'; Fig. 5, Curve 3'). Accordingly, the use of SO_4^{2-} ions instead of Cl^- ions cannot be recommended.

c) CH_3COOH^- ions (in the presence of Cl^- ions) increase the sensitivity of the aluminum electrode to F^- ions. Actually, on adding F^- ions up to a concentration of 0.001 N to a solution of 2 N NaCl + 1 N CH_3COONa, a shift in potential of 0.3 volt is observed (Fig. 2, Curve 2), while on addition of F^- ions up to a concentration of 0.001 N to a solution of 2 N NaCl which does not contain acetate ions, no shift in potential is observed at all (Fig. 3, Curve 2).

When the concentration of F^- ions is increased to 0.001 N, then a shift in potential of 0.3 volt is also observed in the solution of 2 N NaCl which does not contain acetate (Fig. 6, Curve 2). Thus, fluoride activates aluminum at low current densities, chloride prevents complete passivization, thereby increasing the potential range over which the fluoride ions are active, while acetate ions increase the activating effect of fluoride ions in the presence of chloride ions.

From what has been said it follows that the change in potential of the aluminum electrode during potentiometric titration (2, 3, 4) is the result of a combination of the effect of the anions listed, on the electrochemical behavior of the aluminum electrode.

All that has been said above relates to compensation potentiometric titration of aluminum with sodium fluoride solution using the aluminum indicator electrode. In the case of noncompensation titration, both electrodes—aluminum and nichrome—are directly immersed in the solution being titrated and are connected to the poles of a sensitive galvanometer. A resistance of 15-20 thousand ohms is connected in series in the circuit; thus, during titration, a current of the order of $5 \cdot 10^{-5}$ amps • passes through the circuit.

Since the aluminum electrode has a higher negative potential than the nichrome electrode, it is polarized anodically. Consequently, for characterization of the behavior of the aluminum electrode during noncompensation titration, the anodic polarization curve is of significance, and the potential jump at the end-point is determined only by the decrease in the value of the anodic overvoltage.

Thus, the potential jump at the end-point during both compensation and noncompensation titration of aluminum by sodium fluoride, is basically determined by the same reason—acceleration of anodic dissolution of aluminum.

•The potential difference between the aluminum and nichrome electrodes at the moment of compensation, in the absence of a current, is 1 volt as is evident from Fig. 1. Nevertheless, during noncompensation titration this value may decrease a few times because of the polarization of the electrodes.

The mechanism of the shift in potential under the influence of F^- ions is the same for both compensation and noncompensation titration in the case under discussion.

We can establish the limits of applicability of the noncompensation method of titration. During noncompensation titration, the potential of the indicator electrode may remain in equilibrium, or may remain stationary in the case where the current density during titration is less than the exchange current for an equilibrium electrode or less than the self-dissolution current in the case of stationary electrode [6]. The self-dissolution current, as is evident from Fig. 2, is equal to $1.1 \cdot 10^{-5}$ amps/cm^2. In order that the potential of the aluminum electrode should remain stationary even during noncompensation titration, the current density during titration should be less than this value. At current densities greater than 10^{-4} amps/cm^2 (Fig. 2) the activating action of the fluoride ions almost disappears. Accordingly, if, during noncompensation titration, too low a resistance R, less than $R = S \cdot 10{,}000$ ohms is included in the circuit, where S is the surface area of the immersed part of the aluminum electrode, then the potential shift under the influence of fluoride ions at a concentration of 0.001 N is one tenth the shift which is observed during compensation measurements of potential.

All that has been said above relates to the behavior of an aluminum electrode in solutions of salts sodium chloride, acetate, sulfate, and fluoride). Since it is anions which mainly affect the corrosion of aluminum, we first studied their effect on the electrochemical behavior of the aluminum electrode. As mentioned already, the method studied is applicable to the study of heat-resistant alloys, which are made up of a complex mixture of a large number of elements (nickel, chromium, aluminum, molybdenum, tungsten, titanium, iron and other elements present as impurities). A large fraction of the cations present in the alloys possess variable valence. The possibility is not excluded that certain cations also affect the behavior of the aluminum electrode by altering the specific adsorption of the anions. This testifies to the need for an independent study of the question of the effect of cations on the electrochemical behavior of aluminum.

SUMMARY

1. It has been demonstrated that during titration of aluminum salts by sodium fluoride solution using an aluminum-nichrome electrode pair, the potential "shift" at the end-point is caused by a sharp change in the stationary potential of the aluminum electrode (indicator electrode); the potential of the nichrome electrode does not change during titration.

2. In order to establish the nature of the anodic and cathodic processes which determine the stationary potential of the aluminum electrode, and its change during titration, polarization curves were taken for the aluminum electrode in solutions of F^- ions in the presence of Cl^-, CH_3COO^-, and SO_4^{2-} ions for various combinations of these ions, and at concentrations of these ions which correspond to those used for titration of aluminum salts with fluoride.

3. It has been shown that the sharp shift in potential to negative values at the end-point is caused by the accelerating effect of F^- ions on the anodic dissolution of aluminum (by activation of the aluminum electrode); fluoride ions have hardly any effect on cathodic liberation of hydrogen.

4. Cl^- ions prevent complete passivization of the aluminum, and thereby increase the potential range over which F^- ions are active. CH_3COO^- ions increase the sensitivity of the aluminum electrode to F^- ions.

5. The reason for the potential shift of the aluminum electrode at the end-point under the influence of F^- ions is the same for both compensation and noncompensation methods of titration.

6. The limits of the applicability of the noncompensation method have been established with respect to the range of current density in which the fluoride ions exhibit an activating influence on the aluminum electrode.

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QUANTITATIVE DETERMINATION OF THALLIUM AS THE DICHROMATE

COMMUNICATION 1. GRAVIMETRIC AND VOLUMETRIC METHODS

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Quantitative determination of scattered metals, in particular thallium, is connected with considerable difficulties. These difficulties are the result of the necessity of determining scattered metals in the presence of large amounts of the elements accompanying them [1, 2]. When the concentration of thallium in the test material is very low, it is necessary to resort to preliminary chemical enrichment by extraction methods [3-14], cementation [15], chromatography [16-17], precipitation [2, 18-20] or by coprecipitation both by organic [21], and inorganic [22] reagents. In those cases where the concentration of the thallium is sufficient for its direct determination by chemical analytical methods, methods of determining thallium are necessary, which simultaneously ensure its complete separation from accompanying elements.

In the vast literature on the analytical chemistry of thallium, there are no references to methods which would fully satisfy these requirements, despite the fact that methods are known for the determination of thallium which are based on reactions specific for this metal, for example, on precipitation reactions [23-25]. Accordingly, determination of thallium is usually preceded by its separation from interfering elements.

The gravimetric methods which have been suggested in recent years for the determination of thallium [25-27] require reagents which are not readily available, and the use of which in analytical practice meets several difficulties. The best gravimetric method for determination of thallium, as acknowledged by many workers [15, 28-29], is the classical chromate method, which is based on precipitation of thallium from ammoniacal solutions by potassium chromate. Nevertheless, in the presence of other metals, the chromate method is only applicable in certain cases. In such cases the elements which interfere with determination of thallium are kept in solution, either by altering their valence state by means of preliminary oxidation (under conditions which exclude the oxidation of thallium) [28], or by the formation of soluble complexes [18, 19, 28, 30-32]. The manner in which the chromate method is used depends on the nature of the metal which is present, and when several metals are present simultaneously, the method is not always applicable. In order to form soluble complexes of the accompanying elements, it is often necessary to use various complexing agents, the simultaneous use of which is not always possible. Thus, the simultaneous presence of trivalent thallium and iron, which interfere with the determination of univalent thallium in the form of the chromate, excludes the possibility of using an alkali metal cyanide and sulfosalicylic acid which are recommended for complexing them [33].

It was found necessary therefore to study the possibility of carrying out a quantitative determination of thallium as its dichromate during its precipitation from acid solutions. This method of determining thallium could be simultaneously used for its separation from all metals which do not form insoluble compounds under the given conditions.

The possibility of combining the quantitative determination of thallium as its dichromate with its separation from a large number of accompanying elements is of undoubted interest.

Published information on thallium dichromate is scant and dates in the main from the last century [34-39]. Potassium dichromate is a sparingly soluble compound which separates out from solution more readily

the chromate [37]. The similarity of thallium mono- and dichromates gave Carstanjen [37] a basis for suggesting that both compounds could be used for the quantitative determination of thallium.

The microcrystalloscopic method of detecting thallium [40-41] which is based on the formation of crystals of thallium dichromate, is characterized by a limit of identification of about 1 γ at a limiting concentration of 1 : 50,000 [41].

In a paper [42] devoted to the iodometric determination of thallium during its precipitation from alkaline solutions in the form of the monochromate, among other results, results are given of two parallel precipitations of thallium by potassium chromate in the presence of dilute sulfuric acid; in this case 99.53% of the thallium taken was found, when calculations were based on thallium dichromate.

Despite these separate observations, thallium dichromate has been regarded as an unsuitable form for quantitative determination [33]. Forcheimer and Epple [33] tried to precipitate thallium quantitatively as the dichromate from solutions of varying concentration of perchloric acid, but the results obtained were not reproducible. Thallium was only precipitated completely from 1 N perchloric acid when the solution was kept at 0° overnight before filtering. It has been suggested [33] that the high results obtained for the determination of thallium may be explained by the formation of thallium polychromates; and low results by the formation of precipitates consisting of mixtures of thallium mono- and dichromate. These suggestions were probably made because of the absence of published information on the systematic study of thallium chromates. Neither their conditions of formation or their physicochemical properties were known with any certainty.

It has been considered that it is impossible to weigh thallium as its dichromate, Forcheimer and Epple [33] precipitated thallium by means of sodium chromate from a solution of perchloric acid under strictly defined conditons, only for the separation of univalent thallium from trivalent thallium and from iron when all were present simultaneously. For the quantitative determination of thallium, the precipitate of thallium dichromate was converted into thallium monochromate [33] by treating the dichromate on the filter with ammonia solution containing sodium chromate and cyanide.

In order to establish the composition of the thallium chromates, and the concentration limits within which each of them exists, the system $Tl_2CrO_4-CrO_3-H_2O$ was studied by the method of isothermal solubility, while a study was also made of the interactions which occur in the mutual system formed by potassium chromate and sulfuric acid. In the course of this work it was first of all established that, in particular, thallium dichromate Tl_2CrO_7 is an incongruently soluble compound which is completely precipitated by excess chromic anhydride. The results obtained served as a theoretical basis for a detailed development of a method for the quantitative determination of thallium as its dichromate.

In the work described here a study was made of the precipitation of thallium as $Tl_2Cr_2O_7$ from neutral and sulfuric acid solution by means of chromic anhydride.

In order to determine the conditions necessary for the quantitive precipitation of thallium, it was necessary to establish the relationship between the solubility of potassium dichromate and the various ratios of sulfuric acid to chromic anhydride in solution. For this purpose, the same amount of thallium was precipitated by means of chromic anhydride of varying concentration. Precipitation of thallium by chromic anhydride of the same concentration was carried out from a series of sulfuric acid solutions of varying concentrations.

The completeness of precipitation of thallium was determined volumetrically on the basis of the amount of chromic anhydride which had reacted, and by a gravimetric method. The results of these determinations, at the same time, served as a basis for establishing the conditions required for the quantitative determination of thallium by these methods.

The volumetric method, which does not require quantitative separation of the solid phase from the liquid phase, was at the same time a necessary prerequisite for developing a gravimetric method of determining thallium, since, in this case, the problem was complicated by the necessity of washing the precipitate of thallium dichromate in order to preserve its composition.

The Volumetric Method

The method is based on precipitation of thallium as dichromate from neutral or acid solutions by means of chromic anhydride. Thallium was determined on the basis of the amount of chromic anhydride which had thereupon reacted, the concentration of the chromic anhydride having been determined iodometrically.

TABLE 1

Volumetric Determination of Thallium During Its Precipitation as the Dichromate (0.2062 g of Tl taken)

Am't. taken in g per 100 ml		CrO_3 concentration in mother liquor, g/100 ml	Tl found, in g	Error	
CrO_3	H_2SO_4			in mg	in %
0,1535	—	0,0533	0,2049	—1,3	—0,63
0,2371	—	0,1362	0,2062	0,0	0,0
0,2371	0,3	0,1362	0,2062	0,0	0,0
0,2371	1,0	0,1375	0,2036	—2,6	—1,26
0,2371	10,0	0,1407	0,1970	—9,2	—4,46
0,2859	—	0,1850	0,2062	0,0	0,0
0,2859	0,3	0,1851	0,2058	—0,4	—0,19
0,2859	1,0	0,1856	0,2049	—1,3	—0,63
0,3177	—	0,2166	0,2066	+0,4	+0,19
0,3177	0,3	0,2168	0,2062	0,0	0,0
0,3177	1,0	0,2168	0,2062	0,0	0,0
0,3177	10,0	0,2175	0,2048	—1,4	—0,68
0,3337	—	0,2328	0,2062	0,0	0,0
0,3337	0,3	0,2330	0,2058	—0,4	—0,19
0,3367	1,0	0,2359	0,2060	—0,2	—0,10
0,3967	—	0,2960	0,2058	—0,4	—0,19
0,3967	0,3	0,2958	0,2062	0,0	0,0
0,3967	1,0	0,2958	0,2062	0,0	0,0
0,4770	—	0,3761	0,2062	0,0	0,0
0,4770	0,3	0,3761	0,2062	0,0	0,0
0,4770	1,0	0,3761	0,2062	0,0	0,0
0,4902	10,0	0,3900	0,2048	—1,4	—0,68

Earlier [43, 42], thallium had been determined volumetrically by its precipitation from alkaline solutions as the monochromate. This method has been recommended for the quantitative determination of thallium [42].

The drawback of the volumetric method is the indirect determination of thallium, particularly in view of the large difference in the atomic weights of thallium and chromium. Naturally, this drawback is not quite so important in the case of precipitation of thallium as the dichromate, as in the case of its precipitation as the chromate. Nevertheless, even during precipitation of thallium as the dichromate, all the operations must be carried out carefully in the volumetric method.

The original solution of thallium sulfate contained 0.2062 g of thallium in 10 ml. The concentration of chromic anhydride varied within the limits 0.15 to 0.49 g in 100 ml. The sulfuric acid concentration range was 0.3, 1 and 10 g in 100 ml. In those cases where precipitation of thallium was carried out without addition of sulfuric acid, its concentration in the mother liquor was determined on the basis of the amount of material which had reacted, and amounted to 0.05 g per 100 ml of solution.

Aliquot portions were taken and titrated by means of microburets. To 10 ml of the original solution contained in a 100 ml standard flask was added the appropriate amounts of sulfuric acid and standard chromic anhydride solutions. The solution plus the precipitate of thallium dichromate was left overnight. Excess chromic anhydride was then determined on an aliquot of the filtrate. The amount of chromic anhydride which had reacted with thallium was calculated by difference. Each series of precipitations of thallium by the same amount of chromic anhydride was carried out in one standard flask. In order to avoid errors in the determination of the original concentrations of the chromic anhydride, connected with conversion of the various amounts of the standard solution to 100 ml, their concentration was established directly in the same flask as that used for a given series of precipitations. Iodometric determination of chromic anhydride was carried out under conditions ensuring absence of free iodine in sulfuric acid solutions of potassium iodide, this being controlled by carrying out parallel tests. The thiosulfate normality was of the order of 0.05.

The results obtained (Table 1) show that it is possible to carry out a quantitative volumetric determination of thallium during its precipitation as the dichromate from neutral and acid solutions by means of chromic anhydride. In such determinations, the acidity of the solution must be taken into account. When original solution contains up to 0.3 g of sulfuric acid per 100 ml, a content of 0.14 g of chromic anhydride per 100 ml of mother liquor is sufficient to guarantee quantitative precipitation of thallium. When the original solution contains 1 g of sulfuric acid per 100 ml, the thallium is quantitatively precipitated by a chromic anhydride content in the liquid phase of a minimum of 0.22 g CrO_3. Quantitative precipitation of thallium was not observed in the case of solutions containing 10 g of sulfuric acid per 100 ml of solution, for all the chromic anhydride concentrations examined, since, in such cases, a large excess of CrO_3 is required. All the same, volumetric determination of thallium at high concentrations of chromic anhydride cannot guarantee the necessary accuracy.

Accordingly, in practice, it is expedient during the volumetric determination of thallium, to precipitate the latter as its dichromate from solutions containing up to 1 g of sulfuric acid per 100 ml. Under such conditions, the chromic anhydride concentration of the mother liquor should amount to, on an average, about 0.25 g per 100 ml solution.

Gravimetric Method

One of the requisite conditions for using thallium dichromate as a gravimetric form is that it should be quantitatively precipitated from the mother liquor, and that its composition should be constant.

Thallium dichromate is an incongruently soluble compound with a constant composition. It has been established experimentally that this compound is insoluble, particularly in acetone and ethanol. Consequently, it can be assumed that when thallium dichromate is washed by the solvents mentioned, its composition will not change. Quantitative chemical analysis of thallium dichromate is not accurate enough to establish whether or not small changes in its composition do, in fact, occur under such conditions. Accordingly, in order to investigate thallium dichromate washed with acetone or ethanol, use was made in particular of phase differential thermal analysis. A knowledge of the thermal characteristics of thallium dichromate is also essential for enabling a correct choice to be made of the conditions to be used for drying it to constant weight.

Thermographic Study of Thallium Dichromate

Differential thermal investigation of thallium dichromate was carried out on a registering pyrometer of the N. S. Kurnakov type, using a chromel-alumel thermocouple. The thermograms obtained for thallium dichromate washed with acetone and ethanol are shown in Fig. 1. In Fig. 2 are shown respectively the thermogram obtained for thallium dichromate carefully removed from mother liquor by means of a filter, and thallium dichromate washed first with water and then with acetone.

As these thermograms show, the heating curves for thallium dichromate washed with the two solvents (Fig. 1) are exactly the same, and are characterized by the presence of two endothermic effects. As visual observation of the heating process showed, the thermal effect observed at 354-358° corresponds to the first appearance of a liquid phase. The second effect which occurs during the range 358-365° corresponds to complete fusion. This indicates that thallium dichromate melts with decomposition according to a peritectic reaction. Up to the point of incipient melting thallium dichromate is thermally stable.

The heating curve for unwashed thallium dichromate (Fig. 2a) which, consequently, contains some dry residue from the mother liquor, is also similar to the curves already considered; the only difference is that the endothermic effect in this case naturally occurs at a lower temperature.

The similarity of the thermograms obtained indicate that thallium dichromate does not change its composition on washing with acetone or ethanol.

The heating curve for thallium dichromate washed with water (Fig. 2b) is characterized by a small, additional endothermic effect which occurs in the solid state at a temperature of 330-335°. This effect corresponds to a polymorphic transformation of thallium monochromate which is fixed thermographically during its heating. Consequently, the thermogram for thallium dichromate washed with water is a record of the behavior of a mixture of thallium mono- and dichromate. This testifies to decomposition of thallium dichromate as a consequence of incongruent dissolution.

The results obtained show that acetone and ethanol can be used successfully for washing thallium

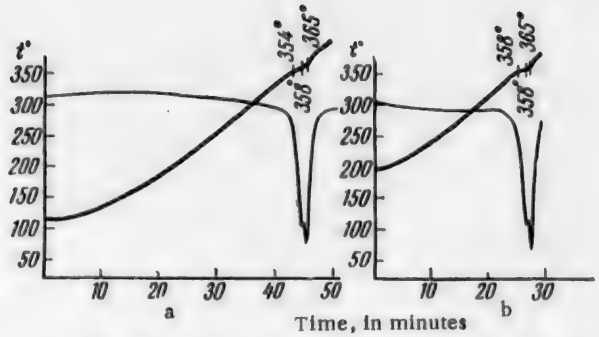

Fig. 1. Heating curves for thallium dichromate washed with acetone (a) and ethanol (b).

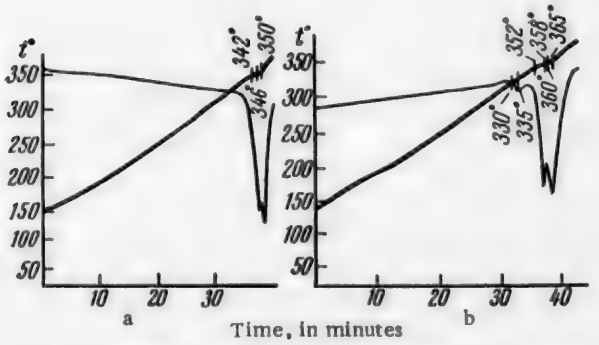

Fig. 2. Heating curves for thallium dichromate removed directly from the mother liquor (a), and washed first with water and then with acetone (b).

dichromate free from chromic anhydride. For this purpose, the concentration of the chromic anhydride should be low so as not to lead to interaction with the organic solvents.

Gravimetric determination of thallium as the dichromate under various precipitation conditions. Ten ml of a solution containing 0.1 g of thallium sulfate was used for the precipitation conditions. Sulfuric acid was added, and a standard solution of chromic anhydride added while the solution was gently warmed. The volume was then made up to 100 ml, the solution was finally left to cool to room temperature and then left overnight.

The sulfuric acid concentration in the various tests was 0.3, 1, 10, 18, and 25 g per 100 ml of solution. In those cases where precipitation was carried out from neutral solutions, the sulfuric acid concentration was determined from the amount of materials which had reacted, and amounted to 0.02 g. The chromic anhydride concentration of the solution was varied from 0.25 to 10 g per 100 ml of solution. The precipitate of thallium dichromate was filtered through a No. 4 crucible. When precipitation was effected by means of chromic anhydride, the concentration of which was greater than 1 g per 100 ml of solution, the precipitate of thallium dichromate was washed beforehand with a solution of chromic anhydride of the same concentration as that in the mother liquor in the case where precipitation was carried out from sulfuric solutions; the precipitate was then washed with a solution containing 1 g of CrO_3 per 100 ml of solution, and then with acetone until the chromate could not be detected iodometrically in the wash liquors. The washed precipitate of thallium dichromate was dried to constant weight at 110-130°.

In those cases where the error in determining thallium was considerable as a result of incomplete precipitation, the solution containing the precipitate was cooled to 1-3° for 2-4 hours.

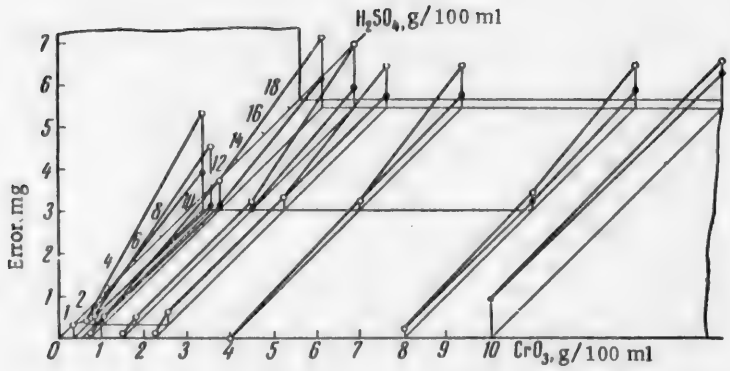

Fig. 3. Relation between the experimental error in determining thallium as its dichromate and the concentration of sulfuric acid and chromic anhydride:
○) $Tl_2Cr_2O_7$ precipitate kept in the mother liquor for 18-20 hours at room temperature; ●) $Tl_2Cr_2O_7$ precipitate kept in the mother liquor for 2-4 hours on cooling to 1-3°.

Results for the determination of thallium as its dichromate are presented in Table 2 and are illustrated by the three-dimensional diagram in Fig. 3.

DISCUSSION OF RESULTS

The work described above testifies to the fact that thallium is quantitatively precipitated in the form of $Tl_2Cr_2O_7$ by the dichromate ion from neutral and acid solutions. In the course of this work, it was established that, in contrast to published results [33], thallium dichromate can be used as a gravimetric form. In addition it has been shown that quantitative determination of thallium as its dichromate can be carried out over a large concentration range of acid in solution and over a wide range of the precipitating chromate.

By using the gravimetric technique of determining thallium, it was found that it was possible to extend the concentration ranges of the sulfuric acid and chromic anhydride considerably, as compared with the concentrations of these reagents used for the volumetric technique during precipitation of thallium dichromate. The experimental error in determining thallium as its dichromate depends on the ratio of sulfuric acid to chromic anhydride in solution. For the quantitative precipitation of thallium, the concentration of acid and chromic anhydride should not exceed certain definite limits established in the course of the present work.

Comparison of the results obtained for thallium (Table 2) when the solution containing the precipitate of thallium dichromate was cooled, and when the solution was kept at room temperature, shows that, as a consequence of the decrease in solubility of the thallium dichromate with the drop in temperature, the experimental error in determining thallium decreases with cooling. When cooling is used, quantitative results are obtained for thallium which are not obtained when cooling is omitted.

The maximum concentration of chromic anhydride which ensures quantitative precipitation of thallium dichromate, both from neutral and sulfuric acid solutions, amounts to approximately 8 g per 100 ml of solution. It is characteristic that when 10 g of chromic anhydride is used, the experimental error, which testifies to incomplete precipitation of thallium, remains almost unchanged even in those cases where precipitation is carried out with cooling (Table 2).

In order to precipitate thallium quantitatively as its dichromate from acid solutions, a greater excess of chromic anhydride is required the higher the acid concentration. When thallium dichromate is precipitated by the same amount of chromic anhydride from solutions with varying sulfuric acid concentrations, the experimental error in determining thallium increases with increasing acid concentration. This is clearly shown in Fig. 3.

The permissible sulfuric acid concentration for determination of thallium as the dichromate amounts to

TABLE 2

Gravimetric Determination of Thallium as Its Dichromate
(0.0810 g of Tl taken)

Amount taken in g per 100 ml		Time of contact of precip. with mother liquor			
		18-20 hrs at room temp.		2-4 hrs on cooling to 1-3°	
CrO_3	H_2SO_4	Tl found,* in g	error in mg	Tl found,* in g	error in mg
0,25	—	0,0808	—0,2	—	—
0,25	0,3	0,0808	—0,2	—	—
0,35	—	0,0807	—0,3	—	—
0,35	0,3	0,0808	—0,2	—	—
0,35	1	0,0809	—0,1	—	—
0,35	10	0,0787	—2,3	0,0801	—0,9
0,40	1	0,0808	—0,2	—	—
0,40	10	0,0786	—2,4	0,0803	—0,7
0,40	18	0,0764	—4,6	0,0777	—3,3
0,55	1	0,0808	—0,2	—	—
0,55	10	0,0795	—1,5	0,0809	—0,1
0,65	1	0,0810	0,0	—	—
0,65	10	0,0797	—1,3	0,0808	—0,2
0,75	—	0,0809	—0,1	—	—
0,75	1	0,0808	—0,2	—	—
0,75	10	0,0803	—0,7	0,0809	—0,1
0,75	18	0,0793	—1,7	0,0803	—0,7
1,5	—	0,0809	—0,1	—	—
1,5	1	0,0809	—0,1	—	—
1,5	10	0,0808	—0,2	0,0810	0,0
1,5	18	0,0795	—1,5	0,0805	—0,5
2,25	—	0,0809	—0,1	—	—
2,25	1	0,0807	—0,3	—	—
2,25	10	0,0807	—0,3	—	—
2,25	18	0,0800	—1,0	0,0807	—0,3
4,0	—	0,0810	0,0	—	—
4,0	10	0,0808	—0,2	—	—
4,0	18	0,0800	—1,0	0,0807	—0,3
8,0	—	0,0808	—0,2	—	—
8,0	10	0,0806	—0,4	0,0808	—0,2
8,0	18	0,0800	—1,0	0,0807	—0,3
10,0	—	0,0802	—0,8	0,0801	—0,9
10,0	18	0,0799	—1,1	0,0802	—0,8
8,0	25	0,0799	—1,1	0,0802	—0,8

*Mean results are given for several cases which were in good agreement with each other.

approximately 18 g/100 ml of solution. Quantitative precipitation of thallium is observed under these conditions only when the solutions are cooled. When thallium dichromate is precipitated from solutions containing 25 g of sulfuric acid per 100 ml by means of chromic anhydride of the maximum permissible concentration, the experimental error obtained indicates incomplete precipitation of thallium, independently of the fact whether the solutions are cooled or not (Table 2).

The experimental error of all determinations, is on the average the same, consequently, the changes in experimental error in thallium determination as a function of the varying concentrations of sulfuric acid and chromic anhydride, are determined by the solubility of thallium dichromate under the given conditions.

The experimental data obtained (Table 2) enables one to choose, for each special case, the necessary concentration of chromic anhydride as a function of the acid concentration of the solution for the quantitative precipitation of thallium.

In general it is best to precipitate thallium as its dichromate from solutions containing up to 10 g of sulfuric acid per 100 ml of solution, by means of chromic anhydride whose concentration amounts to, on an average, 1-2 g per 100 ml of the liquid phase. The precipitate of thallium dichromate plus mother liquor is cooled for 3-4 hours to 0-3°. It is desirable that the total volume of the solution should not exceed 100 ml under these conditions. The thallium dichromate is filtered through a No. 4 crucible and washed with a cooled solution of chromic anhydride whose concentration is the same as that in the original solution, and then with a solution containing 0.25 g of CrO_3 in 100 ml, and finally with acetone or ethanol until no chromate can be detected in the wash liquor. The thallium dichromate is dried to constant weight at 110-130°.

Results of thallium determination by this method are given in Table 3. The sulfuric acid concentration as well as that of chromic anhydride amounted to 1 g per 100 ml in these determinations.

TABLE 3

Quantitative Determination of Thallium as Dichromate

Tl taken, in g	Tl found,* in g	Error, in mg
0.1000	0.0999	−0.1
0.0810	0.0810	0.0
0.0405	0.0405	0.0
0.0081	0.0080	−0.1
0.0040	0.0032	−0.8
0.0040**	0.0039	−0.1

*Mean values of several determinations.

**The precipitate of $Tl_2Cr_2O_7$ plus mother liquor were stood overnight; they were cooled again before filtration.

The results obtained show that when the thallium dichromate precipitate is less than about 0.01 g, it must be kept longer in contact with the mother liquor in order to ensure quantitative precipitation. Accordingly, it is necessary to leave precipitate and solution overnight and keep them cool, and then carry out the determination by the technique developed.

The new method suggested for the quantative determination of thallium as the dichromate has a number of advantages over its determination as the chromate. The main advantage of this method is the possibility of carrying out a direct determination of thallium without preliminary separation from metals which accompany it, in particular from those metals which form hydrated precipitates in alkaline solutions, and which, under the conditions used for the chromate method, require special methods for separating them.

Thallium chromate is precipitated quantitatively over a narrow concentration range of ammonia and potassium chromate [44]. It is possible, however, to vary the concentration of both acid and chromic anhydride over a wide range when thallium is precipitated as the dichromate.

Thallium dichromate separates out from solution more readily and more rapidly than the chromate; it separates out as a heavy, coarse precipitate which is readily filtered and washed. Precipitated thallium dichromate, in contrast to the chromate, need not be kept for such a long time in contact with the mother liquor in order to ensure quantitative precipitation (as long as the thallium concentration is not less than about 0.008 g).

The gravimetric method of determining thallium as the chromate can also be used in microdeterminations [45]. The results given in Table 3 give the basis for suggesting that determination of thallium as the dichromate could also be carried out by a quantitative microchemical analysis, as long as the appropriate conditions are used.

SUMMARY

1. A new method has been developed for the quantitative determination of thallium as the dichromate – $Tl_2Cr_2O_7$; this method is based on precipitation of thallium from neutral or acid solutions by means of chromic anhydride.

Optimum conditions have been established for determination of thallium as the dichromate by indirect volumetric and gravimetric methods.

2. The relation between the experimental error in determining thallium and the concentrations of sulfuric acid and chromic anhydride has been established. The limiting permissible concentrations of these two reagents for the quantitative determination of thallium have been determined.

3. It has been shown that thallium dichromate is an incongrously soluble and incongruously fusible compound.

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THE COLOR REACTIONS OF GALLIUM AND INDIUM SALTS WITH ORGANIC REAGENTS

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Comparatively few reactions are known for gallium and indium which can be used for developing photometric methods for determining these elements; accordingly, up to the present, only 8-hydroxyquinoline, quinalizarin, etc. [1] which have comparatively low specificity, have been used. The reactions of various hydroxyanthraquinones, and hydroxyquinones of the benzene and naphthalene series with indium salts have already been studied [2], nevertheless their characteristics and sensitivities were not discussed. The object of the work described here was the search for, and the study of, color (and fluorescent) reactions for gallium and indium.

Reactions with 2,2' Dihydroxyazo Dyes

o,o'-Dihydroxyazo dyes react with many metals to form compounds whose color differs from that of the reagent itself; in this connection therefore, they are used as indicators during titration with complexons. In the case of aluminum and gallium, the simultaneous appearance of an orange or red fluorescence with the change in color is characteristic. The analytical applicability and the composition of the compounds formed have been studied several times [3-6].

We have synthesized a number of representatives of this group of dyes, using 1-amino-2-naphthol-4- sulfonic acid and picramic acid as the first component of the azo compound, while phenols capable of supplying a hydroxyl group in the ortho position to the azo group on coupling were used as the second component.

The capacity of the synthesized dyes to react with gallium and indium salts at various pH values was studied, while the sensitivity of the reactions and their behavior toward Group III elements were also examined. In the course of this work it was established that some of these dyes give a fluorescent reaction with gallium salts which is more sensitive than those with dyes already known.

Table 1 contains details of the composition and formula of the dyes prepared, as well as the colors given by aluminum, gallium, and indium, and the sensitivity of the detection of gallium on the basis of observations of the orange-red illumination obtained on irradiating with an analytical quartz lamp. The reactions were carried out in the presence of buffer mixtures with a pH of 3-4.

As is evident from Table 1, the sensitivity of the detection of gallium with some of the newly synthesized compounds (No. 3, 4) is higher than with reagents which are already known (No. 1, 2). Reagent No. 3 is particularly suitable; the reaction with this reagent is carried on 2 ml of test solution in the presence of 2 ml of alcohol, a few drops of chloracetate buffer mixture* with a pH of 3.0, and a few drops of the dye solution (0.1% in alcohol being added. It should be pointed out that when gallium salts are used, the fluorescence is brighter in the presence of alcohol; in the case of aluminum salts a bright luminescence can be observed in the absence of alcohol, although in this case too, addition of alcohol enhances the intensity of the luminescence.

Dyes based on picramic acid either do not give a fluorescence or give a weak one; some of these dyes react with high sensitivity with gallium salts to give a variable color (Nos. 6, 8); it is characteristic that aluminum does not give a similar effect.

*A mixture of equal volumes of 0.5 M monochloroacetic acid and its ammonium salt.

TABLE 1

Reactions of o,o'-Dihydroxyazo Dyes with Aluminum, Gallium, and Indium Salts

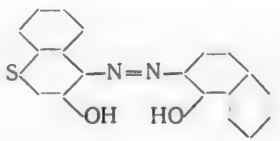
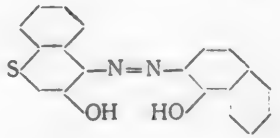
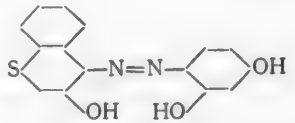
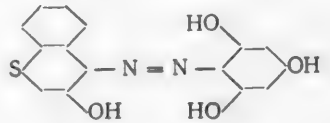
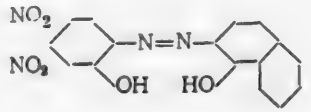
Expt. No.	Dye*	Color of solution with dye and with salts				Sensitivity of gallium detection, in γ
		Ga	Al	Zn	blank	
1	4-Sulfo-2-hydroxynaphthalene-1-azo-2,1-hydroxynaphthalene 	Violet	Red-violet			0,5
2	4-Sulfo-2-hydroxynaphthalene-1-azo-1,2-hydroxynaphthalene 	"	"			1,0
3	4-Sulfo-2-hydroxynaphthalene-1-azo-4-1,3-dihydroxybenzene 	Red	Red	Dark-red		0,05—0,1
4	4-Sulfo-2-hydroxynaphthalene-1-azo-4-1,3,5-trihydroxybenzene 	Raspberry	Brown-yellow	Red	Yellow	0,2
5	1-Hydroxy-4,6-dinitrobenzene-2-azo-2,1-hydroxynaphthalene 		Greyish-violet			—

TABLE 1 (continued)

Expt. No.	Dye*	Color of solution with dye and with salts				Sensitivity of gallium detection, in γ
		Ga	Al	Zn	blank	
6	1-Hydroxy-4,6-dinitrobenzene-2-azo-1,2-hydroxynaphthalene	Red	Yellow-rose			—
7	1-Hydroxy-4,6-dinitrobenzene-2-azo-4-1,3-dihydroxybenzene		Brownish-yellow			—
8	1-Hydroxy-4,6-dinitrobenzene-2-azo-1,2-hydroxynaphthalene-3,6-disulfonic acid	Raspberry	Red-yellow	Rose	Red-yellow	0,2
9	1-Hydroxy-4,6-dinitrobenzene-2-azo-2-1,8-dihydroxynaphthalene-3,6-disulfonic acid	Violet	Green-blue	Violet	Red-violet	—

*S stands for the SO_3H group.

TABLE 2

Reactions of Various Compounds with Aluminum, Gallium, and Indium Salts

Compound	Medium in which reaction was carried out	Color and reaction sensitivity with salts of			
		Ga	Al	In	Blank
The azo dye from H acid and resorcinol	Weak hydrochloric acid	Rose 1 – 2 γ	Rose	Yellow	Yellow
p-Nitrobenzeneazopyrocathechol	Acetic acid	Red 1 γ	Yellow-orange	Yellow	Light-yellow
Schiff base from o-amino-2-naphthosulfonic acid and salicylaldehyde	Weak hydrochloric acid	Yellow 1 γ	Yellow	Colorless	Colorless
Schiff base from H-acid and salicylaldehyde	Weak hydrochloric acid	Yellow 1 γ	Yellow	Colorless	Colorless
Gallein	Ditto	Red violet 0.2 γ			Rose-yellow
Dihydroxyfluorescein	Acetic acid, pH 4.5	Raspberry 0.5 γ	Orange		Yellow
o-Hydroxyphenylfluorone	Acetic acid plus pyridine	Raspberry 1 γ	Rose-Yellow	Raspberry	Rose-yellow
Diphenylcarbazone	Hydrochloric acid plus pyridine	–	–	Violet 0.5 γ	Colorless

Of considerable interest is the reaction of aluminum with dye No. 9, in view of the very sharp color change from red-violet to blue-green.

Dyes No. 4 and 8 can be used for detecting indium; the sensitivity of the reaction with the first of these was found to be 1 γ of Zn in 2 ml of solution (on adding 3 drops of an acetate buffer with a pH of 4).

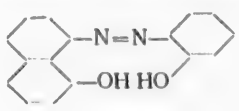
None of the elements tested – In, Mn, Ni, Co, Fe, Ti, Cr^{III} and Zn – give a similar illumination to gallium apart from aluminum. As for color changes, they are also obtained with many of the cations tested; thus, salts of Cr^{III}, Ni, Co, Ti, Zn and Fe^{II} react with dyes No. 4 and 6, while dye No. 8 reacts with salts of these metals as well as with those of chromium. Consequently, before carrying out reactions for gallium and indium, these elements should be separated from accompanying elements.

Of the synthesized reagents, 4-sulfo-2-hydroxynaphthalene-1-azo-1,3-dihydroxybenzene proved suitable for the quantitative determination of gallium in coal, ores, and industrial wastes with a sensitivity of some hundredths part of a percent [7].

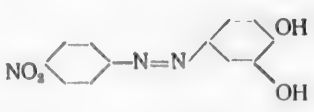
Reactions for Gallium and Indium with Some Other Compounds Containing Hydroxyl Groups

The reactivity of a series of colored organic compounds containing oxygen towards gallium, indium, and some other elements was studied; these compounds included:

1) Azo dyes containing two hydroxyl groups—one in the ortho and the other in the peri position (in the naphthalene series) with respect to the azo group (I).



(I)

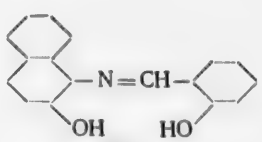


(II)

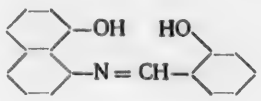
These dyes which are derivatives of diazotized "H" or "K" acids and resorcinol or orcin, are reagents for boric acid in weakly acid solutions [8].

2) An azo dye containing two hydroxyl groups in the ortho position with respect to each other, namely p-nitrobenzoazopyrocatechol (II). Derivatives of this type, as already established, are reactive toward germanium, zirconium, and gallium [9], and other elements.

3) Schiff Bases containing hydroxyl groups in the ortho (III) and peri positions (IV) with respect to the azomethine group



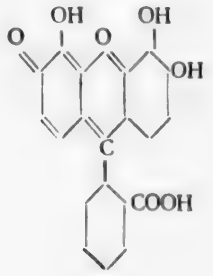
(III)



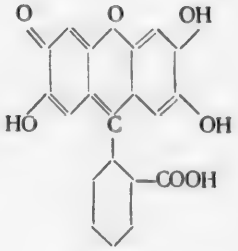
(IV)

In certain cases it is known that azomethine compounds of similar configuration react with the same elements as the corresponding azo dyes [10].

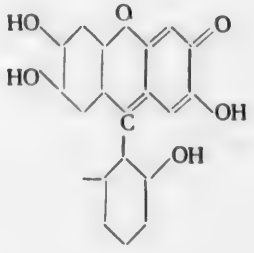
4) Dyes which are derivatives of fluorone–gallein (V), dihydroxyfluorescein (VI), and o-hydroxyphenyl-9-2,3,7-trihydroxy-6-fluorone (VII)



(V)

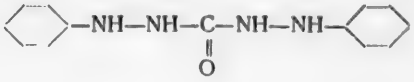


(VI)



(VII)

5) And, finally, a compound which does not belong to the group of dyes considered, namely diphenylcarbazone



The reactions of these compounds are given in Table 2.

As the results in Table 2 show, the compounds tested react mainly with gallium salts, only the last two react with indium. Although the sensitivity of the reactions is fairly high, the specificity is small; in addition to gallium, aluminum and some other elements also react with the first six compounds. For example, manganese, iron, and titanium salts react with the first dye, while iron and titanium salts react with the second.

Salts of trivalent iron (brown color) and zirconium (yellow precipitate with reagent No. 4) interfere with the reactions with the Schiff's bases. Iron, lead, bismuth, copper, tin, and zirconium salts interfere with reactions with the fluorone derivatives, while in the case of hydroxyphenylfluorone, zinc, nickel, and cobalt salts as well as other salts interfere in addition to salts of the elements already mentioned. Ferrous salts as well as indium salts interfere with diphenylcarbazone but ferric salts do not interfere, while nickel, cobalt, zinc, lead, and zirconium salts also interfere; salts of Al, Ti^{IV}, Cr^{III}, Mn, Bi, Cu, Cd, As^{III}, Sb and Sn^{IV} do not react.

All the same, despite their limited specificity, some of these reactions could be used under conditions where removal from accompanying elements is carried out prior to the photometric determination of indium or gallium; these dyes could also be used as indicators during the complexonometric titration of these elements. In particular, diphenylcarbazone is suitable for the determination of indium in germanium, the sensitivity in this case being of the order of some hundredths of a percent [11].

Color Reactions for Indium Based on Its Capacity to Form Complex Anions

The capacity of indium to form complex anions has been used to a comparatively small extent in analysis; it has only been used in certain microchemical reactions—with urotropine or quinoline [12], and with sparteine in the presence of thiocyanate [13]. The chemistry underlying these reactions consists of the formation of sparingly soluble salts of the organic bases with complex indium-thiocyanic acid. Formation of the indium iodide of methyl violet was suggested recently for the isolation of small amounts of indium by precipitation with organic coprecipitants [14].

TABLE 3

Reactions of Indium in the Form of a Complex Anion

Reagent	Added to the solution	Sensitivity, in γ, In	Behavior of other elements		
			do not react	give the same reaction	interfere
Rhodamine C	1 g KI; 1 *N* HCl, 4 drops	5	Ga, Al, Ti, Ni, Co, Zn, Sn	Cr, Mn, Hg^{++}, Pb, Cd	Bi, Cu, Sb, Fe
	1 ml 40% KSCN	5	Al, Mn, Ni, Hg, As, Sb	Ga, Ti, Cr, Co,	Fe, Bi, Cu
Methyl violet	1 ml 50% KI; 1 *N* HCl, 2 drops	2	Ga, Al, Ti, Cr, Mn, Ni, Co, Zn, As, Sb^{III}, Sn^{IV}	Zn, Pb, Cd, Sn^{IV} Hg, Bi, Cd	Fe, Cu
	1 ml 40% KSCN; 1 *N* HCl, 3 drops	0,2	Ga, Al, Ti, Cr, Mn, Ni, Pb, As, Sb, Sn^{IV}	Co, Zn, Hg, Cd	Fe, Cu

Since during the use of the basic organic dyes—methyl violet [15] and rhodamine C [16]—colored solid phase reactions may occur which can be used for determining many metals, we studied the suitability of these reagents for detecting indium by means of color reactions.

To 2 ml of a solution of an indium salt was added a halide (thiocyanate) of an alkali metal in sufficient amount to give a concentration of 13-50%, this was followed by the dye solution. Where necessary, the solution was acidified with a few drops of 1 N hydrochloric acid. The color obtained was compared with the color of a control solution.

Chloride, bromide, iodide, and thiocyanate were tried as complexing agents, but only iodide and thiocyanate proved suitable. When methyl violet was used, the color of the control was green, while the test solution containing indium had a violet color and a precipitate of the same color was formed; when rhodamine C was used, the control solution was of a pale-lilac color, almost colorless, while that of the test solution was violet.

Results of these reactions are given in Table 3.

As these results show, the reaction with iodide is more specific than that with thiocyanate. The specificity of the reaction for indium can be enhanced by using appropriate masking agents; thus, in the reaction with thiocyanate and rhodamine, zinc and cadmium can be masked by addition of potassium cyanide and pyridine.

SUMMARY

A study has been made of various color reactions given by certain organic compounds with gallium and

indium; these compounds included o,o'-dihydroxyazo dyes, azo dyes containing hydroxy groups in other positions, and Schiff bases and phenylfluorone derivatives; a study has also been made of a number of reactions for indium based on the capacity of indium to form complex anions. It has been established that some of these compounds give more sensitive reactions with gallium and indium than representatives of this group which have been studied previously. Thus, gallium can be detected more sensitively by the fluorescence it gives with the dye 4-sulfo-2-hydroxynaphthalene-1-azo-1'-2,4-dihydroxybenzene; indium can be detected by means of a color reaction with diphenylcarbazone and by means of reactions with some other reagents. Results are given for the sensitivity and specificity of the reactions.

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•In Russian.

•• [8] omitted in the Russian — Publisher's note.

•••Original Russian pagination. See C. B. Translation.

DETERMINATION OF DI- AND TRIVALENT TITANIUM IN SLAGS CONTAINING METALLIC AND DIVALENT IRON

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In the first communication [1] a method was described for the determination of total lower oxides of titanium in slags containing divalent iron. The method consists essentially of decomposing the slag in acid in the presence of salts of quinquevalent vanadium and trivalent iron, which oxidize the di- and trivalent titanium, and the divalent iron present.

Excess of oxidizing agent is titrated with a solution of Mohr's salt. Divalent iron is determined on a separate aliquot. The next stage which we undertook was the development of a method for the separate determination of di- and trivalent titanium in slags containing metallic and divalent iron.

When an aliquot of slag is decomposed in orthophosphoric acid on heating in an atmosphere of carbon dioxide, divalent titanium is oxidized to the trivalent state which is stable under these conditions. During the decomposition of an aliquot of slag in a mixture of HF + H_2SO_4 in the presence of excess of a solution of ferric ammonium alum, divalent iron is formed in an amount which is equivalent to the total di- and trivalent titanium present.

In order to check on the stability of trivalent titanium on heating in a solution of orthophosphoric acid, parallel determinations of trivalent titanium in slags were carried out by dissolving aliquots in orthophosphoric acid.

TABLE 1

Reproducibility of Determinations of Ti_2O_3 in Slags (in %)

Sample No.	Parallel determinations	Mean
2412	12,50; 12,75; 12,50; 12,78	12,63±0,13
2405	18,11; 18,27; 18,12; 18,47; 18,24	18,24±0,10
2406	20,57; 20,95; 20,94; 20,24; 20,42	20,62±0,26
2411	40,98; 41,07; 40,71; 40,27	40,76±0,27
Ti_2O_3 oxide	90,51; 92,60; 90,72; 91,62	91,36±0,75

As the results in Table 1 show, the parallel determinations show good reproducibility; the mean deviation does not exceed 1% (relative). When the content of trivalent titanium as determined by decomposition of an aliquot in orthophosphoric acid corresponds to its actual amount, then on summing the results of the determinations of all the components the total should not exceed 100%.

In order to confirm the correctness of this conclusion, some anosovites were analyzed and the trivalent titanium content also determined (Table 2).

From the results given in Table 2 it follows that only summation of the contents of Ti^{III} and Ti^{IV} permits

TABLE 2

Complete Analysis of Anosovites (in %)

Sample No.	Ti_2O_3 parallel determinations	Ti_2O_3 mean	SiO_2	Fe_2O_3	FeO	Fe_{metal}	TiO_2	Al_2O_3	MnO	MgO	CaO	Total I	TiO (Total titanium)	Total II
115	26,96; 27,30	27,13±0,17	3,07	—	2,33	—	53,03	6,20	0,60	8,13	—	100,49	83,17	103,50
119	28,34; 28,00	28,17±0,17	—	—	1,34	0,21	53,10	7,60	0,57	9,05	—	100,04	84,40	103,17
124	26,26; 25,92	26,09±0,17	3,20	—	2,99	—	54,40	5,65	0,58	6,97		99,88	83,38	102,77

one to get a total of 100% for full analysis of a sample. When the content of Ti^{III} is not taken into account, and titanium is determined as Ti^{IV}, the sum for complete analysis of an analysis is 2.8-3.5% greater than the normal sum (100%), and amounts to 102.77-103.5%. This difference will be larger the greater the Ti^{III} content of the sample. Thus, these results indirectly confirm that the trivalent titanium content established by dissolving the sample in orthophosphoric acid is the correct one.

In addition, Ti^{III} was determined in anosovites by two methods: by dissolving the sample in orthophosphoric acid, and in a mixture of hydrofluoric and sulfuric acids in the presence of excess ferric ammonium alum. When the Ti^{III} is not oxidized in the solution of orthophosphoric acid on warming, the results obtained by the two methods mentioned should coincide.

The results obtained are given in Table 3.

It follows from the results given in Table 3 that those obtained for the determination of trivalent titanium by dissolving the sample in orthophosphoric acid are in good agreement with those obtained by dissolving the sample in a mixture of hydrofluoric and sulfuric acids in the presence of ferric ammonium alum; they agree to an accuracy of 1% relative, this testifies to the stability of trivalent titanium in orthophosphoric acid on heating.

The last two columns in Table 3 contain the results for the increases in weight which were determined on heating a sample of slag to constant weight at 900° in a stream of oxygen, and the increases in weight calculated on the basis of the content of trivalent titanium, metallic and divalent iron.

The experimental and theoretical increases in weight are in good agreement; this confirms the reliability of the methods for determining trivalent titanium, metallic and divalent iron.

These results again confirm the stability of trivalent titanium in orthophosphoric acid on heating.

Divalent titanium is unstable in a solution of orthophosphoric acid, and is quantitatively oxidized to the trivalent state. Thus, during determination of divalent titanium by the two methods: dissolving an aliquot in orthophosphoric acid, and also dissolving an aliquot in a mixture of hydrofluoric and sulfuric acids in the presence of ferric ammonium alum, the following results were obtained (Table 4).

It follows from the results given in Table 4 that during titration of the solution obtained by decomposing the oxide by heating in orthophosphoric acid, the number of milliliters of standard solution used was only half of that used during titration of the solution obtained after decomposing an aliquot in a mixture of hydrofluoric and sulfuric acids in the presence of ferric ammonium alum. Actually, during dissolution of a sample in orthophosphoric acid, divalent titanium is oxidized to give an equivalent amount of trivalent titanium. Thus, the change $Ti^{II} \rightarrow Ti^{III}$ is not registered, and the number of milliliters used up in the titration only corresponds to the change $Ti^{II} \rightarrow Ti^{IV}$.

When an aliquot of test material is dissolved in a mixture of hydrofluoric and sulfuric acids in the presence of ferric ammonium

TABLE 3

Comparison of Results for the Determination of Trivalent Titanium by Two Methods

Sample No.	TiO_3			Fe metal	FeO	Increase in weight (experimental)	Increase in weight (calculated)
	sample dissolved in H_3PO_4	sample dissolved in HF + H_2SO_4 in the presence of alum	mean				
2407 Slag	23.88	24.21	24.04 ± 0.17	1.04	0.48	3.12	3.23
119 Slag	24.42	24.27	24.35 ± 0.08	1.53	2.33	3.89	3.89
119 Anosovite	28.17	28.15	28.16 ± 0.01	0.21	1.34	3.57	3.53
2411 Slag	40.76	39.78	40.27 ± 0.49	1.10	0.37	4.97	5.03

TABLE 4

Results of an Analysis of an Oxide Containing 89.30 TiO and 9.7 TiO_2 (in %)

Sample dissolved in H_3PO_4		Sample dissolved in a mixture of HF + + H_2SO_4 in the presence of alum	
milliliters of 0.1 N alum solution used for titration	mean	milliliters of 0.1 N $KMnO_4$ solution used for titration	mean
14.0; 14.1; 13.9	14.0 ± 0.10	28.0; 28.0; 27.8	27.9 ± 0.10

alum, divalent titanium is oxidized to the trivalent state, which, in turn, is further oxidized to quadrivalent titanium.

Accordingly, in this case, both the transition of Ti^{II} to Ti^{III} and of Ti^{III} to Ti^{IV} are registered, and the number of milliliters of titrant corresponds to the two stages of the oxidation of titanium.

Thus, as a basis of the method which has been developed for the separate determination of di- and trivalent titanium in slags, use has been made of the difference in the stability of titanium in these two valence states in a solution of orthophosphoric acid on heating. A description is given below of an analytical procedure for the determination of di- and trivalent titanium, and of metallic and divalent iron in slags.

1. Determination of trivalent titanium which represents total Ti^{III} present in the slag, and Ti^{II} oxidized to Ti^{III} during decomposition in orthophosphoric acid. 0.2-0.5 g of slag is placed in a 250 ml conical flask and 25-35 ml of orthophosphoric acid sp.gr. 1.7 added, a stream of carbon dioxide is then passed through the mixture for 15 minutes, and the sample decomposed by heating for 20-30 minutes with constant agitation. After decomposition is complete, the flask and the solution obtained is cooled and 50 ml of sulfuric acid 1 : 4 added, the solution is then cooled again to room temperature in a carbon dioxide atmosphere. The stream of carbon diozide is then switched off and 20 ml of a 40% aqueous solution of ammonium thiocyanate added, the solution is then titrated with 0.05 N ferric ammonium alum solution until the color of the solution changes from yellow to orange. Let the volume of ferric ammonium alum solution used for titration of total titanium (III) be denoted by V_1.

2. Determination of total Ti^{II} and Ti^{III} present in the slag. 0.2-0.5 g of slag is placed in a 100 ml conical flask and 15 ml of a 10% aqueous solution of $CuSO_4$ added, the mixture is diluted with distilled water to 50 ml and the whole boiled for 15-20 minutes in a stream of CO_2 in order to dissolve the metallic iron. Solution and precipitate are then filtered through a filter paper (red band) and the precipitate washed 4-5 times with hot water. Twenty ml of H_2SO_4 1 : 3 is added to the filtrate followed by 15 ml of H_3PO_4 sp.gr. 1.7, the total volume should be 150-200 ml; the solution is then titrated with 0.01 N ammonium vanadate using barium diphenylaminesulfonate as indicator, the color change being from light blue to blue; metallic iron is thereby

TABLE 5

Determination of TiO, Ti_2O_3, Metallic and Divalent Iron (in %)

Sample number	TiO			Ti_2O_3			F_{metal}			FeO		
	parallel determinations		mean	parallel determinations		mean	parallel determinations		mean	parallel determinations		mean
11 (Slag)	1,00;	0,92	0,96±0,04	12,27;	12,19	12,23±0,04	1,31;	1,25	1,28±0,03	2,00;	1,90	1,95±0,05
9 (Slag)	1,97;	1,87	1,92±0,05	12,83;	13,00	12,94±0,06	1,45;	1,34	1,39±0,05	1,99;	1,86	1,93±0,05
80 (Anosovite)	2,37;	2,10	2,24±0,13	56,27;	55,88	56,08±0,20	—	—	—	—	—	—
75 (Anosovite)	6,09;	5,42	5,75±0,34	55,28;	54,71	55,00±0,28	2,06;	2,08	2,03±0,04	0,70;	0,70	0,75±0,06
50 (Slag)	20,21;	20,53	20,37±0,16	2,63;	3,00	2,80±0,18		1,96			0,84	

determined. The filter paper and precipitate were treated with a hydrochloric acid solution of ferric chloride for 5 minutes in the cold in order to dissolve metallic copper. The precipitate is then transferred onto a filter paper (red band) and carefully washed with hot water, and then washed several times with cold 5% sulfuric acid. The precipitate is washed off the filter paper with a strong stream of hot water into a platinum basin 11 cm in diameter; excess ferric ammonium alum solution is then added, followed by 5 ml of sulfuric acid sp.gr. 1.84; the platinum basin is covered with another platinum basin 9 cm in diameter and a stream of carbon dioxide turned on for 15 minutes. Ten ml of hydrofluoric acid is then added, the total volume of the solution at this stage should be about 50 ml; the whole is thoroughly mixed and then heated for 20-30 minutes until the slag is completely dissolved. The solution is cooled in carbon dioxide stream and 20 ml of a saturated solution of boric acid added in order to complex the fluoride ions. The solution is transferred to a 500 ml flask containing 30-50 ml of distilled water, and 5 ml of sulfuric acid sp.gr. 1.84; divalent iron which is equivalent to total di- and trivalent titanium is then titrated with 0.05 N $KMnO_4$. Let the volume of $KMnO_4$ used for titration be denoted by V_2.

A correction must be applied to the titration result for the amount of divalent iron already present in the test material; in order to establish this correction, divalent iron should be determined on a separate aliquot by the following method.

0.5 g of slag is treated with cupric sulfate by the method described above in order to remove metallic iron. The slag is then decomposed in a platinum basin by heating with a mixture of 5 ml of sulfuric acid (sp.gr. 1.84), and 10 ml of hydrofluoric acid in an atmosphere of carbon dioxide, the total volume of the solution in the basin is made up to 50 ml with distilled water. When decomposition of the slag is complete the solution is transferred to a 500 ml flask containing 20 ml of a saturated solution of boric acid, 5 ml of sulfuric acid (sp.gr. 1.84), and 15 ml of orthophosphoric acid (sp.gr. 1.7); the total volume of the solution should be 150-200 ml. One ml of a 5% solution of sodium tungstate is added and residual, reduced titanium, which has not been completely oxidized during decomposition in hydrofluoric acid, titrated with a potassium permanganate solution until the blue color disappears [1]. Divalent iron is then titrated in the same solution with 0.01 N ammonium vanadate, using barium diphenylaminesulfonate as indicator.

Let the volume of ammonium vanadate used for titrating FeO present in the slag be denoted by V_3. The true volume of $KMnO_4$ used for titrating the divalent iron equivalent to total Ti^{II} and Ti^{III} is then given by the difference $V_2 - V_3$, let this difference be denoted by V_0. The volumes of the standard solutions of ferric ammonium alum, potassium permanganate, and ammonium vanadate used for titration are reduced to unit weight and normality. Then $(V_0 - V_1)$ is the

volume of standard solution which is equivalent to Ti^{II}, while $V_1 - (V_0 - V_1) = (2V_1 - V_0)$ is the volume of standard solution equivalent to Ti^{III}.

The percentage contents of TiO and Ti_2O_3 are calculated by means of the formulas:

$$\% \text{ TiO} = \frac{63.9 \cdot N (V_0 - V_1)}{1000 \cdot n} 100,$$

$$\% \text{ Ti}_2\text{O}_3 = \frac{143.8 \cdot V (2V_1 - V_0)}{2 \cdot 1000 \cdot n} 100,$$

where N is the normality of the standard solution and n is the weight of sample.

Blanks must be carried out.

Table 5 contains results for the determination of TiO, Ti_2O_3, metallic iron and divalent iron in slags and anosovites.

The results obtained are reproducible. The accuracy (mean deviation of duplicates) amounts to 0.5-1.0% (relative) for titanium contents of 10 to 60%, and to 6% (relative) for titanium contents of 1-5%; this is fully satisfactory for establishing in what form the titanium exists in the slags.

The author wishes to thank A. I. Ponomareva and B. N. Melent'eva for help and advice in preparing the article for the press.

SUMMARY

A method has been developed for the separate determination of di- and trivalent titanium in slags containing metallic and divalent iron.

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DETERMINATION OF URANIUM BY MEANS OF POTASSIUM IODATE

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Methods based on the formation of sparingly soluble compounds of quadrivalent uranium which are stable in mineral media are of considerable interest from an analytical point of view. The main drawback of such methods, however, is the complexity of the subsequent determination of uranium [1-5].

In the work described here which was carried out in 1952, the iodate method suggested earlier by Chernikhov and Uspenskii [6, 7] for the determination of thorium, zirconium, and cerium, was used for the direct determination of uranium. In the course of this work the optimum conditions for formation of a precipitate of the iodate of quadrivalent uranium with a definite composition were established, as well as the possibility of determining uranium gravimetrically and titrimetrically.

Preliminary tests showed that it is impossible to prepare a precipitate of constant composition when Kaufman's method is used [5]; according to this method, to a test solution containing 4-5% sulfuric acid by volume, an equal volume of 10% KIO_3 in 10% H_2SO_4 is added followed by twice the volume of 0.8% solution of KIO_3 in 2% H_2SO_4. It was found necessary to decrease the amount of 10% KIO_3 solution; thus, for contents of 5 mg and more of uranium, it was necessary to add it in the proportion of 1 : 2 to the volume of test solution taken, while in the presence of smaller amounts of uranium (1-2 mg) it was found necessary to add it in the proportion of 2 : 3 with respect to the test solution. The 0.8% solution of KIO_3 should be added, as indicated already, in an amount which is double that of the original volume of solution; this volume was 15-30 ml in all our tests. Quadrivalent uranium was prepared electrolytically on a mercury cathode [8].

The uranium iodate precipitate was filtered through a No. 4 glass crucible and washed with a dilute solution of potassium iodate (0.4% KIO_3 in 1% H_2SO_4) and then with alcohol and ether. The precipitate washed in this way readily came to constant weight at a temperature of 100-120°, and did not decompose on heating to 170°. It should be pointed out that when the precipitate was only washed with potassium iodate solution and alcohol, decomposition was observed as low as 60°.

The uranium content of the precipitate was determined by permanganatometric titration and by calcining to U_3O_8. Iodate was determined iodometrically after dissolving the precipitate in sulfuric acid and oxidizing the uranium with potassium permanganate to the sexivalent state.

The absence of potassium in the precipitate was established by a microcrystalloscopic reaction with chloroplatinate after decomposition of the precipitate and removal of uranium. On the basis of the weight of the precipitate and the uranium and iodate content which were determined experimentally, it was established that no water of crystallization is present in the precipitate dried at 110-120°.

The analytical results are presented in Table 1.

Accordingly, the composition of the precipitate of uranium iodate precipitated under the conditions outlined above, corresponds to the formula $U(IO_3)_4$. The conversion factor to uranium is 0.2539. It has been shown in this way that it is possible to determine uranium (IV) gravimetrically as its iodate. Table 2 contains results of determinations of various amounts of uranium.

Iodometric titration can be used for the titrimetric determination of uranium. For this purpose, the

TABLE 1

Results of the Analysis of Precipitated Uranium Iodate (calculated value of U for $U(IO_3)_4$, 25.39%; IO_3 content = 74.61%)

U found, in %		IO_3 found, in %	
	25.65		74.64
	25.38		74.15
	25.31		74.56
	25.16		74.88
	25.42		75.02
Mean	25.38	Mean	74.65

TABLE 2

Gravimetric Determination of Uranium as Iodate (mean of 3-4 determinations)

Uranium taken, in mg	Weight of precipitate, in mg	Uranium found, in mg	Error	
			in mg	in %
13.50	52.9	13.43	−0.07	−0.5
13.50	53.8	13.64	+0.14	+1.0
6.75	26.2	6.65	−0.10	−1.5
6.75	26.8	6.80	+0.05	+0.7
1.686	6.513*	1.654	−0.032	−1.9
1.686	6.661*	1.691	+0.005	+0.3
1.686	6.714*	1.704	+0.018	+1.1
			Mean	±1.0

*Weighed on a microbalance.

TABLE 3

Titrimetric Determination of Uranium as Iodate

Uranium taken, in mg	$Na_2S_2O_3$ used up, in ml	Uranium found, in mg	Error	
			in mg	in %
6.750	12.40*	6.685	−0.065	−1.0
6.750	12.60*	6.790	+0.040	+0.6
3.375	6.30*	3.395	+0.020	+0.6
2.680	20.70**	2.692	+0.012	+0.4
2.680	20.50**	2.667	−0.013	−0.5
1.686	13.10**	1.704	+0.018	+1.0
1.686	12.85**	1.671	−0.015	−0.9
1.349	10.35**	1.346	−0.003	−0.2
1.349	10.40**	1.353	+0.004	+0.3
			Mean	±0.6

*0.04981 N $Na_2S_2O_3$ used.

**0.01201N $Na_2S_2O_3$ used.

uranium iodate precipitate which had been precipitated and washed as indicated above, was dissolved in 20 ml of 10% sulfuric acid and 20 ml of 5% potassium iodide solution added, the liberated iodine was then titrated with thiosulfate. Special experiments showed that part of the iodine liberated reacts with quadrivalent uranium:

$U^{4+} + I_2 + 2H_2O = UO_2^{2+} + 2I^- + 4H^+$. Thus one atom of uranium corresponds to 22 gram equivalents of iodine.

Results of titrimetric determinations of uranium are given in Table 3.

Copper and molybdenum do not form iodates under the conditions used for precipitating uranium iodate; moreover, they can be removed by electrolysis on a mercury cathode.

TABLE 4

Titrimetric Determination of Uranium in the Presence of Aluminum

Ratio of U : Al	Taken, in mg		Uranium found, in mg	Error	
	aluminum	uranium		in mg	in %
1:10	70	6.745	6.734	−0.011	−0.16
1:10	14.2	1.349	1.358	+0.009	+0.66
1:50	330	6.745	6.675	−0.070	−1.3
1:50	72	1.349	1.387	+0.038	+2.7
1:75	550	6.745	6.419	−0.326	−4.8
1:100	660	6.745	6.088	−0.657	−9.5
1:100	135	1.349	1.165	−0.184	−14.0

Vanadium, which is reduced during the electrolysis process, is not precipitated either during precipitation of uranium iodate.

As the results in Table 4 show, aluminum present in amounts which are 50 times that of uranium, does not interfere. Nevertheless, when the amount of aluminum present is greater than this, appreciable losses of uranium are observed; this could be explained, presumably, by a salt effect.

Divalent iron, even at low concentrations, leads to incomplete precipitation of uranium. For example when the iron content is 0.5 mg, the experimental error is 10-15%. This phenomenon can be explained by the fact that the trivalent iron formed oxidizes iron to the sexivalent state.

SUMMARY

Conditions have been established for precipitating uranium as the iodate of quadrivalent uranium with a constant composition expressed by the formula $U(IO_3)_4$. It has been found that the iodate method can be used for both the titrimetric and gravimetric determination of uranium. The effect of certain elements on the accuracy of uranium determination has been studied. It has been found that it is possible to determine uranium in the presence of aluminum. Iron must be removed beforehand.

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THE SEPARATION OF URANIUM AND VANADIUM

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Many methods are known for the separation of uranium and vanadium [1-4], but several of them give incomplete separation, and require several reprecipitations. The disadvantage of the separation methods is particularly obvious in those cases where the reactions on which the separations are based are carried out in solutions which are almost neutral. The difficulty encountered in trying to separate these two elements suggest that there may be some interaction between uranium and vanadium. This possibility is indirectly confirmed by the existence of a number of natural minerals—uranovanadates—and by the ease with which uranovanadates can be synthesized from aqueous solutions under laboratory conditions.

In a previous paper [5] we showed that in aqueous solution, quinquevalent vanadium and sexivalent uranium form a complex uranovanadium anion. The acid corresponding to this anion, as well as the salts of the acid, are sparingly soluble in water, and are deposited from solution at a concentration as low as $5 \cdot 10^{-5}$ g-ion/liter, the composition of the precipitate formed varying with changes in the ratio of U : V in solution. When the solution contains excess uranium, the ratio U : V in the precipitate increases to 1.5 : 1; while, on the other hand, when vanadium is present in excess, this ratio decreases to 1 : 2 and less. We should like to point out that we analyzed the precipitates 24 hours after pouring together the appropriate solutions; this time interval was necessary for complete formation of the complex anions in solution.

The possibility of synthesizing compounds with a low ratio of U : V in the absence of a whole number value for the share of the vanadium, gave the basis for assuming that there occurs a gradual substitution of OH groups in the complex by metavanadate anions VO_3^- right up to the formation of a completely substituted uranyltrimetavanadate.

Depending on the ratio of uranium to vanadium in the solution one might expect that the precipitates formed will be a compound of one of the following three complex anions:

Uranyldihydroxymetavanadate $[UO_2(OH)_2VO_3]^-$

Uranylhydroxydimetavanadate $[UO_2(OH)(VO_3)_2]^-$

Uranyltrimetavanadate $[UO_2(VO_3)_3]^-$.

The composition of some natural minerals—the uranovanadates—is in good agreement with this assumption.

The formation of similar types of complex compounds undoubtedly may be a source of error in trying to carry out reactions for separating uranium and vanadium. Accordingly, in order to evaluate methods for the analytical separation of these elements, it is desirable to know the solubility of uranovanadates and the pH ranges within which they are stable.

The work described here was devoted to the study of these problems. In this connection, since it was impossible in practice to separate the free acids from the solutions in which they were formed, we confined ourselves to their ammonium salts during the solubility studies.

The effect of the composition of the solution, and the contact time of solution and precipitate, on the composition of the precipitate. In order to establish the effect of increasing the proportion of vanadium in solution, and of the total concentration of the reactants, on the composition of the precipitate, solutions with varying U : V ratios and different uranium concentrations were prepared. The solutions were placed in flasks which were tightly sealed with rubber stoppers well smeared with grease; the contact time between solution and the precipitate formed in it was varied for each solution.

The uranium and vanadium contents of the precipitates were determined photometrically by the peroxide method, after removing the precipitates from the solution by filtering them through No. 2 ultrafilters, and dissolving them in dilute sulfuric acid.

The results obtained (Table 1) show that increasing the vanadium concentration in solution to a value which is three times that of uranium slows down the formation of uranyltrimetavanadate. Even under favorable values of U : V, in solution however, formation of uranyltrimetavanadate proceeds slowly, and requires not less than three months for uranium concentrations in the original solution of $5 \cdot 10^{-4}$ g-atom/liter, and about 6 months when the initial uranium concentration of the solution is ten times as much.*

TABLE 1

Uranium taken, in g-atom/liter	Atomic ratio U : V					
	in the original solution	in the precipitate after standing for:				
		24 hours	10 days	one month	three months	six months
$5 \cdot 10^{-4}$	1 : 3	1 : 2.5	1 : 2.6	1 : 2.9	1 : 3	1 : 3
	1 : 5	1 : 2.5	1 : 2.6	1 : 2.7	1 : 2.9	1 : 3
$5 \cdot 10^{-3}$	1 : 3	1 : 2.5	1 : 2.7	1 : 2.8	1 : 2.9	1 : 3
	1 : 5	No precipitate	1 : 1.5	1 : 1.5	1 : 1.5	1 : 1.5

TABLE 2

Uranium Concentration of the Original Solution, in g-atom/liter $5 \cdot 10^{-4}$

Ratio U : V, in g-atom		
in the original solution	in the precipitate	
	after heating	in the cold
1 : 1	1 : 1	1 : 1
1 : 2	1 : 2	1 : 1.8
1 : 3	1 : 3	1 : 2.5
1 : 5	1 : 3	1 : 2.6

The experiments described were carried out at room temperature. We tried to increase the rate of formation of uranyltrimetavanadate by heating the solution containing uranium and vanadium. Qualitative observations showed that the precipitate is formed more rapidly under these conditions.

Table 2 contains results obtained during determination of the proportion of U : V in precipitates obtained on heating the solution to the boiling point (the precipitates were analyzed one hour after pouring the solutions together). For comparison, results are given for precipitates obtained under similar conditions at room temperature (the analysis was carried out 24 hours after pouring the original solutions together).

It is obvious that heating accelerates formation of the end product of the substitution of OH^- by VO_3^- in the complex uranovanadium anion.

The reason for this speeding up could be either an increase in the solubility of the uranylvanadate containing the least vanadium, or a weakening of the U — OH bond with increasing temperature. It is possible, of course, that both factors operate at once.

*This is connected with polymerization of vanadate [2] at such high concentrations. The monoform of metavanadic acid enters into the composition of the complex. The appearance of polymers lowers its concentration, and initially slows down (c_V about $n \cdot 10^{-3}$ g-atom/liter), and then prevents formation of the trimetavanadate (c_V about $2.5 \cdot 10^{-2}$ g-atom/liter).

TABLE 3

Ratio of U : V in the original solution		Concentration of acid or alkali (Normality)•									
		HCl					NaOH				
		10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
1 : 1	pH solution	3.1	3.0	2.8	2.1	1.1	3.2	3.4	4.0	4.9	6.4
	U : V in the precipitate	1 : 1.1	1 : 1.15	1 : 1	1 : 1.1	No precipitate	1 : 1.1	1 : 1	1 : 1.15	1 : 1	No precipitate
1 : 2	pH solution	3.3	2.9	2.8	2.3	1.4	3.3	3.5	4.1	5.0	6.6
	U : V in the precipitate	1 : 1.9	1 : 1.89	1 : 1.9	1 : 1.85	No precipitate	1 : 1.9	1 : 1.9	1 : 1.9	1 : 1.9	No precipitate
1 : 3	pH solution	3.3	3.3	3.3	2.8	2.2	3.7	3.9	4.2	5.8	6.7
	U : V in the precipitate	1 : 2.6	1 : 2.5	1 : 2.5	1 : 2.5	No precipitate	1 : 2.5	1 : 2.5	1 : 2.5	1 : 2.6	No precipitate
1 : 5	pH solution	4.3	4.3	4.1	3.2	2.1	3.74	4.5	5.4	5.6	6.7
	U : V in the precipitate	1 : 2.8	1 : 2.8	1 : 2.8	1 : 2.8	No precipitate	1 : 2.8	1 : 2.8	1 : 2.8	1 : 2.8	No precipitate

•The normality indicated here would be that obtained when the alkali (acid) is added to distilled water. The true concentration of free H^+ ions in the solution over the precipitate is expressed by the pH values.

TABLE 4

Percentage content			Total percent	Molecular ratio
U_3O_8	V_2O_5	Loss on calcination		$U_3O_8 : V_2O_5 : H_2O$
68.1	22.2	9.8	100.0	1 : 1.5 : 6.1
54.4	34.2	11.3	100.6	1 : 3 : 9
44.7	42.4	12.6	99.7	1 : 4.5 : 12.1

TABLE 5

Percentage content					Molecular ratio
U_3O_8	V_2O_5	Loss on calcination	NH_3	H_2O	$U_3O_8 : U_2O_5 : NH_3 : H_2O$
68.2	22.1	9.61	4.1	5.4	1 : 1.5 : 3 : 3.5
53.5	34.6	11.86	3.17	8.7	1 : 3 : 3 : 7.6
44.3	42.4	13.5	2.9	10.5	1 : 4.5 : 3 : 11.1

TABLE 6

Time of agitation, in hours	Uranium concentration in the solvent, in μg/ml		
	I	II	III
1	0.096	0.041	0.024
2	0.110	0.042	0.023
3	0.100	0.041	0.023
4	0.100	—	—
Molar solubility (on an uranium basis)	$4.2 \cdot 10^{-7}$	$1.7 \cdot 10^{-7}$	$9.7 \cdot 10^{-8}$
Lp	$1.7 \cdot 10^{-13}$	$2.9 \cdot 10^{-14}$	$9.6 \cdot 10^{-15}$

The change in the composition of the uranylvanadates is related to changes in the amount of OH in the complex. It could be postulated that the composition of these compounds should depend on the pH of the medium. Table 3 contains the results of a series of experiments on the precipitation of uranylvanadates from solutions with a constant uranium concentration ($5 \cdot 10^{-4}$ g-atom U/liter) and variable vanadium concentration, when the pH of the solution was varied. The precipitates were analyzed 24 hours after pouring the solutions together.

From these results it is clear that precipitates are formed within the wide pH limits of 2.2-6.5; under these conditions their composition does not depend on the hydrogen ion concentration.

Precipitates which had separated out on heating solutions containing only uranyl nitrate and ammonium vanadate were also analyzed, as well as precipitates formed on heating solutions containing ammonium chloride as well as uranyl nitrate and ammonium vanadate. In the first instance solutions with ratios of uranium to vanadium of 1 : 1, 1 : 2, and 2 : 1 were prepared. After heating the solutions to the boiling point, the precipitates were filtered through a No. 2 ultrafiltrate, and washed with weakly acidified water, they were then dried at 102° in a thermostat and analyzed. The mean results of five determinations are given in Table 4.

On the basis of the analyses the formulas of these compounds were calculated:

1. $2UO_3 \cdot V_2O_5 \cdot 6H_2O$ or $H[UO_2(OH)_2VO_3]H_2O$
2. $UO_3 \cdot V_2O_5 \cdot 3H_2O$ or $H[UO_2(OH)(VO_3)_2]2H_2O$
3. $2UO_3 \cdot 3V_2O_5 \cdot 8H_2O$ or $H[UO_2(VO_3)_3]4H_2O$.

The precipitates contained a small amount of ammonia (< 0.8 %); it is possible that hydrogen was partially replaced by ammonium ions.

In a similar way compounds were synthesized in the presence of ammonium chloride, the concentration of the latter being 10^{-2} N. Results of the analyses of these compounds are given in Table 5. The following compounds were prepared in this way:

1. $2UO_3 \cdot V_2O_5 \cdot 2NH_3 \cdot 2.2H_2O$ or $NH_4[UO_2(OH)_2VO_3]$
2. $UO_3 \cdot V_2O_5 \cdot NH_3 \cdot 2.2H_2O$ or $NH_4[UO_2(OH)(VO_3)_2] \cdot 1.5H_2O$
3. $2UO_2 \cdot 3V_2O_5 \cdot 2NH_3 \cdot 7H_2O$ or $NH_4[UO_2(VO_3)_3] \cdot 3.5H_2O$.

Solubility of ammonium uranylvanadates. The solubility of the following three ammonium uranylvanadates: $NH_4[UO_2(OH)_2VO_3]$ (I); $NH_4[UO_2(OH)(VO_3)_2] \cdot 1.5H_2O$ (II); $NH_4[UO_2(VO_3)_3] \cdot 3.5H_2O$ (III), was determined in water and in aqueous solutions of ammonium chloride and hydrochloric acid at 18 and 50°.

The solubility determinations were made on the basis of uranium whose concentration was determined by the luminescent bead method according to Bykova's technique [6], using a LIuF-51 photometer.

The solubility was studied isothermally; the temperature was kept constant by means of a contact thermometer with an accuracy of ± 0.02° at 18°, and ± 0.1° at 50°. The test salt was placed in a vessel with a mercury seal and a screw-shaped stirrer connected to an electric motor. The stirring rate was 600-700 revolutions per minute. Fifty ml of solvent was introduced into the vessel.

TABLE 7

Time of agitation, in hours	Uranium concentration in solution, in μg/ml					
	18°			50°		
	I	II	III	I	II	III
1	0.065	0.008	0.016	0.12	0.069	0.040
2	0.100	0.013	0.032	0.15	0.071	0.041
3	0.150	0.050	0.038	0.15	0.069	0.041
4	0.180	0.069	0.037	0.16	0.070	0.040
5	0.180	0.070	0.037	–	0.071	–
6	0.180	0.070	0.038	–	–	–
Molar solubility (based on uranium)	$7.5 \cdot 10^{-7}$	$3.0 \cdot 10^{-7}$	$1.6 \cdot 10^{-7}$	$6.5 \cdot 10^{-7}$	$3.0 \cdot 10^{-7}$	$1.7 \cdot 10^{-7}$
Lp	$5.5 \cdot 10^{-13}$	$9.0 \cdot 10^{-14}$	$2.6 \cdot 10^{-14}$	$4.2 \cdot 10^{-13}$	$9.0 \cdot 10^{-14}$	$2.8 \cdot 10^{-14}$

Samples of solution were taken every hour; the aliquot was filtered through a No. 3 filter crucible, the filtrate was sucked off on a Komovskii pump. All these operations were carried out at constant temperature.

Table 6 contains the results obtained for the solubility of ammonium uranylvanadates in water at 18°, while Table 7 contains the results for the solubility in a 10^{-2} solution of ammonium chloride at 18 and 50°.

As these results show, the solubilities of the ammonium uranylvanadates in water and in dilute aqueous solutions of ammonium chloride are very similar and hardly change at all with temperature over the range 18-50°. This shows that the reason for the speeding up of the formation of the uranyltrimetavanadate on heating is connected with the greater stability of the bond U – VO_3 as compared with U – OH. The latter is

TABLE 8

Time of agitation, in hours	Uranium concentration in the solvent, in μg/ml			
	10^{-4} N HCl			10^{-3} N HCl
	I	II	III	I
1	0.146	0.058	0.033	0.10
2	0.225	0.121	0.071	0.25
3	0.267	0.120	0.076	0.51
4	–	0.120	0.077	0.60
5	–	0.120	0.077	0.62
6	0.265	–	–	0.62
7	–	–	–	–
8	–	–	–	–
9	0.266			
Molar solubility (based on uranium)	$1.1 \cdot 10^{-6}$	$5.0 \cdot 10^{-7}$	$3.2 \cdot 10^{-7}$	$2.5 \cdot 10^{-5}$
Lp	$1.2 \cdot 10^{-12}$	$2.5 \cdot 10^{-13}$	$1.0 \cdot 10^{-13}$	$6.2 \cdot 10^{-10}$

weakened on heating and accelerates the substitution of OH ions by VO_3^-. Determination of solubility at higher temperatures was complicated by the fact that the finely dispersed precipitates could not be removed from the hot solution by means of a filter even when a No. 4 filter crucible was used.

Table 8 contains the results of the solubility of the same salts in hydrochloric acid at 18°.

It is clear from this Table that the solubility of the salts in 10^{-4} N HCl is somewhat greater than in NH_4Cl solution. Increasing the acid concentration to 10^{-3} N increased the solubility even more, as was to be expected. Addition of acid affects the secondary dissociation of the salt according to the scheme

$$[UO_2(OH)_2VO_3]^- \rightleftharpoons UO_2(OH)_2 + VO_3^-,$$

the equilibrium state of which is strongly dependent on the pH of the solution since the pH determines the state of the uranyl and vanadium ions [5].

DISCUSSION OF RESULTS

The results obtained testify to the very low solubility of ammonium uranylvanadates (of the order of the solubility of the silver halides), this solubility decreasing in the sequence $NH_4[VO_2 \cdot (OH)_2VO_3] \rightarrow NH_4[UO_2(VO_3)_3]$. The solubility of the salts of these acids with divalent metals is, apparently, of the same order ($L_pBa[UO_2(OH)_2 \cdot VO_3]_2 \sim 10^{-21}$). The low solubility of the uranylvanadates which leads to coprecipitation of vanadium during the precipitation of various uranium compounds, is particularly clearly manifested in those cases where separations are carried out at a pH of 2.2-7.

The results we have obtained give a basis for postulating that separation of uranium and vanadium should be most complete in strongly acid or in strongly alkali solutions. Thus, under optimum conditions, separation can be effected by means of cupferron. The phosphate separation is less successful, since this method involves addition of a large amount of salts to the solution, and this facilitates deposition of uranovanadates in the precipitate; the hydrogen ion concentration in solution during all the separation operations is very close to that which is used for the interaction of uranium and vanadium. Furthermore, the solubility of the uranyl phosphates in ammonium chloride solutions is almost one order higher than that of ammonium uranyltrivanadate—the salt which is most probably formed during separation of uranium from excess vanadium. The addition of excess ammonium phosphate, and the alkalinification of the solution shifts the equilibrium according to the law of mass-action toward the formation of phosphates, and, in this way, favors the separation of uranium and vanadium.

Thus, separation of uranium (VI) and vanadium (V) in neutral and weakly acid media is not reliable. During their separation, one should presumably avoid long standing of weakly acid or neutral solutions containing these ions, particularly in the presence of "neutral" salts. It should also be remembered that heating strongly accelerates complex formation, and the formation of precipitates.

Where it is necessary to separate uranium from large amounts of the alkali and alkaline-earth metals, it is possible to use the low solubility of the uraniumvanadate salts of the chosen cation; this technique is especially useful for the isolation of small amounts of uranium from very dilute solutions. It is sufficient to add a 1-3 fold excess of ammonium vanadate to such a solution, and then acidify the solution (to pH 3.5-7) and finally heat to the boil.

SUMMARY

1. It has been found that the uranovanadic acids are precipitated at a pH of 2.2-6.5. Within these pH limits the composition of the precipitate is independent of hydrogen ion concentration.

2. It has been shown that the formation of ammonium uranyltrimetavanadate is a long process. At uranium concentrations of $5 \cdot 10^{-4}$ g·atom/liter, and a three fold excess of vanadium, it takes as long as three months at room temperature, while in the presence of a five-fold excess of vanadium the process takes six months. Heating the solution to the boil sharply increases the rate of formation of uranyltrimetavanadate.

3. The solubility of ammonium uranyldihydroxymetavanadate, uranlyhydroxydimetavanadate, and uranyltrivanadate has been determined.

4. Conditions have been established by means of which it should be possible to achieve the most complete separation of uranium (VI) and vanadium (V).

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SPECTROCHEMICAL DETERMINATION OF TANTALUM IN ZIRCONIUM

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Determination of small amounts of tantalum (< 0.01%) in zirconium is accompanied by a number of difficulties. Photometric methods of determining tantalum are not really suitable because of their relatively low sensitivity (40 γ in 20 ml). Further, during the photometric determination of tantalum by means of pyrogallic acid [1] titanium interferes to a considerable extent. The sensitivity of direct spectrographic determination of tantalum in zirconium is also low, and, according to our studies, amounts to $1 \cdot 10^{-2}$ %. The sensitivity of the spectrographic determination of tantalum can be increased by separating it beforehand from zirconium, the best method for separation being extraction of tantalum in the form of a fluoride complex [2-4]. For separating tantalum from titanium, Chernikhov, Tramm, and Pevzner [5] used extraction of the fluoride compounds with cyclohexanone (sp. gr. 0.95, b. p. 156°).

Our experiments have shown that extraction with cyclohexanone permits quantitative separation of tantalum from zirconium, while the small amounts of tantalum in the extract can be reliably determined spectrographically.

Separation of tantalum from zirconium by extraction with cyclohexanone. A standard tantalum solution (containing 0.5 mg of tantalum / ml) was prepared by fusing 0.0611 g of tantalum pentoxide with potassium pyrosulfate. The melt was dissolved in 2 M sulfuric acid containing 1-1.5 ml of hydrofluoric acid, the solution being made up to 100 ml with 2 M sulfuric acid.

Tantalum was extracted from 2-4 M sulfuric acid with cyclohexanone; three extractions were sufficient for the quantitative extraction of tantalum into the organic phase for a ratio of 1 : 1 for the aqueous and organic phases (Tables 1 and 2).

Experiments on the separation of comparatively large amounts of tantalum from zirconium (Table 3) showed that, under the conditions chosen, tantalum passes over completely into the organic phase, while almost all the zirconium remains in the aqueous solution.

For the spectrographic determination of small amounts of tantalum in the extract, it is sufficient to concentrate the tantalum solution to a small volume (2-3 ml) to ensure a high sensitivity. For this purpose it was found most convenient to distil the cyclohexanone as an azeotrope with water boiling at 90°; by using this technique, resinification of cyclohexanone is avoided.

The fact that no tantalum was lost during extraction and azeotropic distillation was established by using the radioactive isotope Ta^{182} (Table 4).

Choice of conditions for the spectrographic determination of tantalum in solution. For the spectrographic determination of impurities in small volumes of solution, the technique involving preliminary deposition and drying of the solution on the front of the electrode surface is widely used. The thin layer of deposit thereby obtained is then ignited in a spark or arc discharge.

Our experiments showed that the highest sensitivity is achieved during spark excitation of the spectrum and by using carbon electrodes 3-3.5 mm in diameter. Using these conditions, the sensitivity is approximately three times the sensitivity achieved by means of carbon electrodes of normal diameter (6 mm); when the ISP-22 spectrograph is used, this sensitivity amounts to 0.1 γ.

TABLE 1

Extraction of Tantalum by Means of Cyclohexanone at Various Sulfuric Acid Concentrations (1.0 mg of Ta taken)

H_2SO_4 concentration, in M	Ta determined, in mg	Error, in mg	Number of extractions
2	0.95	−0.05	3
2	1.00	0.0	4
3	1.04	+0.04	3
4	1.00	0.0	4
4	1.07	+0.07	4

TABLE 2

Amount of Tantalum in the Various Fractions During Extraction with Cyclohexanone

Tantalum taken, in mg	Tantalum extracted, in mg				Error, in mg
	fractions				
	I	II	III	total	
1	0.8	0.25	0.05	1.1	+0.1
1	0.85	0.10	0.05	1.0	0.0
2	1.6	0.25	0.075	1.93	−0.07

TABLE 3

Separation of Tantalum from Zirconium by Extraction with Cyclohexanone (100 mg Zr taken)

Tantalum taken, in mg	Amount detected in the extract, in mg	
	zirconium*	tantalum
1.0	0.014	1.0
1.0	0.016	0.95
2.0	0.07	2.0
2.0	0.023	2.0
1.0	0.011	1.0

*Zirconium was determined photometrically in the extract using arsenazo [6].

TABLE 4

Behavior of Tantalum During Extraction (Ta^{182} with 2420 impulses/minute taken)

Determination of tantalum, in impulses/minute				
in the rejected acid solution	in the organic phase after distillation	in the aqueous layer after distillation	in the main solution	total
3	–	9	2390	2402
5	3	11	2370	2389
8	–	20	2300	2328
–	8	6	2480	2494

TABLE 5

Passage of Tantalum into the Discharge as a Function of the Time of Spark Burning

Duration of spark discharge, in seconds	Intensity of the analytical line Ta 2685.1 A*		Amount of Ta^{182} on the electrodes, in impulses/minute*	
	electrode size, in mm			
	3	6	3	6
0	–	–	2820	2855
10	32.6	10.9	1012	1940
30	13.2	7.81	533	1241
50	6.00	6.50	290	947
70	2.54	5.75	176	693
90	–	4.80	84	517
110	–	3.53	–	349
130	–	2.11	–	270

*Mean of three measurements.

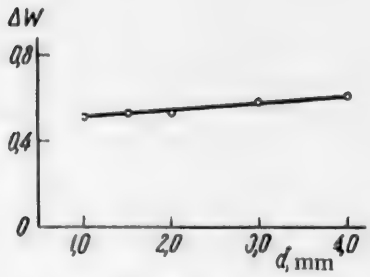

Fig. 1. Effect of the interelectrode gap on the valve of W.

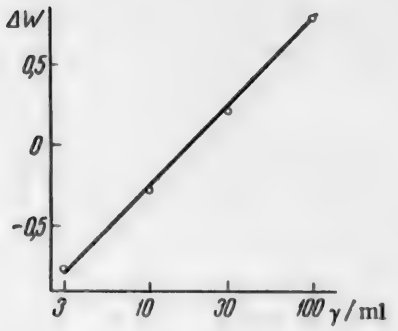

Fig. 2. Calibration curve.

TABLE 6

Effect of Acid Concentration on Tantalum Determination

H_2SO_4 concentration, in %	Ta introduced, γ/ml	Ta found, in γ/ml*
5	50	46
10	50	53
20	50	52
40	50	57

*Mean of three measurements.

TABLE 7

Effect of Zirconium on Tantalum Determination

Zr content, in γ/ml	Ta introduced, in γ/ml	Ta found, in γ/ml*
0	10	10.0
5	10	9.5
10	10	9.5
20	10	9.4
30	10	9.8

*Mean of six measurements.

TABLE 8

Results for the Spectrographic Determination of Tantalum in Zirconium

Ta introduced, in γ/ml	Ta found, in γ/ml*	Relative error, in %	Ta introduced, in γ/ml	Ta found, in γ/ml*	Relative error, in %
14	14	0	25	21	16
16	11	21	16	16	0
20	26	30	16	18	12
20	20	0	12	8.0	33
7.5	8.0	7	16	11	31
7.5	9.0	20	16	12	25
10	12	20	12	11	8
10	14	40	15	13	13
25	24	4	15	14	7

*Mean of three measurements.

Studies of the "burning off" of the tantalum from the electrodes by means of a moving photographic plate, and also by means of radioactive Ta^{182}, showed that the increase in sensitivity in the case of a 3 mm electrode is the result of a more rapid passage of the tantalum into the discharge (Table 5). When the 3 mm electrodes were used, the main part of the tantalum passed into the discharge in the course of 40-50 seconds, while when 6 mm electrodes were used, the time taken was 100-120 seconds. Since the exposure time for registration of the spectra on "Type II" plates amounts to 20 seconds (any further increases in exposure time

TABLE 9

Spectrochemical and Photometric Determination of Tantalum in Zirconium

Sample No.	Found, in %	
	by the spectrochemical method	by the photometric method
1	0.26	0.24
2	0.16	0.17
3	0.17	0.17
4	0.035	0.035

lead to a significant increase in the background), the increase in sensitivity observed in the case of 3 mm electrodes is readily comprehended.

The sensitivity of the determination of tantalum by means of its most intense line Ta 2685 1 A is also essentially dependent on the parameters of the spark generator. The optimum parameters for the spark generator IG-2 are: capacity 0.02 μF, self-inductance 0.01 μH.

The value of the interelectrode gap does not show any strong effect on sensitivity; in our case this was 2 mm.

In order to increase the accuracy of the determination of tantalum in the extract, an internal standard was used, this was molybdenum, which was added to the test materials and to the standards in an amount of 15 γ/ml. The line Mo 2688.0 A served as a reference line. The analytical pair of lines Ta 2685.1 A / Mo 2688.0 A, as our experiments showed, is fully suitable for quantitative determinations. Changes in the interelectrode gap have almost no effect on the blackening difference (Fig. 1).

Standard solutions containing 3, 10, 30, and 100 γ of Ta/ml were prepared from a stock solution with a concentration of 0.5 mg/ml. Appropriate aliquots of the stock solution were transferred to 25 ml standard flask to which molybdenum was then added at the rate of 15 γ/ml, and the volume made up to the mark with water.

The calibration curve (Fig. 2) is best constructed within the coordinates logarithm c, ΔW (W is the transformed blackening), Within these coordinates, the curve is linear over the range 3-100 γ/ml Ta. Treatment of 15 photographic plates showed that the curves obtained for different plates are only insignificantly displaced parallel to one another. This indicates that it should be possible to use the method of a control standard when the conditions for exciting the spectra and treating the plates are strictly observed.

During extraction of tantalum, insignificant amounts of sulfuric acid (5-10%) and zirconium (Table 3) also pass into the organic phase. Accordingly, it was necessary to investigate the possible effect of the acidity of the concentrate, and the amount of zirconium in it, on the spectrographic results.

Determination of tantalum in solutions whose sulfuric acid content varied from 5 to 40%, showed (Table 6) that the acidity has almost no effect on the accuracy of the spectrographic analysis. All the same, the sensitivity of the determination is somewhat lower (approximately half as much for a 50% sulfuric acid content).

Similarily, zirconium contents of up to 30 γ/ml have no effect on tantalum determination (see Table 7).

The method developed for the spectrographic determination of tantalum in zirconium was used for the analysis of a series of zirconium samples to which known amounts of tantalum had been added (Table 8).

Determination of various concentrations of tantalum in zirconium by spectrochemical and photometric methods gave results which were in satisfactory agreement with each other (Table 9).

On the basis of the results given in Table 8, the accuracy of the method was evaluated as 20% (mean arithmetic error). The sensitivity of the spectrographic method of determining tantalum in sulfuric acid solution amounts to 3 γ/ml when two drops of the solution are placed on the electrodes. Accordingly, when 1 g of zirconium is taken and the extract obtained is evaporated to 2-3 ml, it is possible to determine about $1 \cdot 10^{-3}$ % of tantalum in the zirconium. The sensitivity can be increased by increasing the weight of the aliquot taken and by evaporating the extract to a smaller volume.

The authors wish to thank L. V. Lipis for valuable advice and for his continued interest in the work.

SUMMARY

A spectrochemical method is suggested for the determination of small amounts (< 0.01%) of tantalum in zirconium; the method is based on the separation of tantalum from zirconium by extraction of the fluoride complex of tantalum from a sulfuric acid medium by means of cyclohexanone; this is followed by spectrographic determination of tantalum in the extract after removal of the cyclohexanone as an azeotropic mixture with water. Molybdenum is used as an internal standard.

The method permits determination of down to $1 \cdot 10^{-3}$% of tantalum in 1 g of zirconium with a mean arithmetic error of about 20% relative.

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DETERMINATION OF CALCIUM, MAGNESIUM, ALUMINUM, SILICON, AND TIN IN REFINED PLATINUM AND PALLADIUM

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Spectrographic determination of small amounts of Ca, Mg, Al, Si, and Sn in refined platinum and palladium is best carried out in solution, since the preparation of standards in the form of melts is a difficult problem, while standard powders do not guarantee the requisite accuracy in the case being discussed. During work with solutions we adopted the technique described by S. A. Borovik and T. F. Borovik-Romanova [1].

Using water twice distilled in quartz vessels and acidified with distilled hydrochloric acid, a number of solutions were prepared from analyzed, chemically pure spectroscopic quality $CaSO_4$, $Mg(NH_4)_2$, $(SO_4)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $SnCl_2 \cdot 2H_2O$; the solutions prepared contained Ca, Mg, Al, Si, and Sn in amounts ranging from $3 \cdot 10^{-6}$ to $1 \cdot 10^{-2}$%. The solution of sodium silicate was prepared by dissolving a melt of chemically pure silica and sodium carbonate in water; the silicon concentration of the solution obtained was determined chemically.

The solutions were placed successively in a sprayer, into which fresh solution was fed every minute during the course of the experiment. An a.c. arc was used. The spectra were photographed on a Hilger spectrograph (the average model) using NIKFI (Type 2) plates.

The following pairs of lines were used for constructing calibration curves.

Ca II	– 3933.67	–	Pt I	3966.36
Mg II	– 2802.7	–	Pt I	2803.24
Al I	– 3961.52	–	Pt I	3966.36
Si I	– 2881.58	–	Pt I	2893.87
Sn I	– 3034.12	–	Pt I	3036.43

The internal standard used was the background in the neighborhood of the line being photographed [2]. Scattering of the points was insignificant over the concentration range $3 \cdot 10^{-6}$ to $1 \cdot 10^{-2}$%. A solution containing 1% of platinum was then prepared, the platinum compound used was platinum cis-dinitrodichlorodiammine– $(NH_3NO_2)_2Cl_2Pt$ (Blomstrand's salt); this salt was recrystallized twice, nevertheless small amounts of calcium could still be detected in it, and this could not be removed despite several recrystallizations. Accordingly, corrections were applied to the results obtained, for the amount of this impurity; this was determined by extrapolation.

Standard solutions with concentrations of 0.0001 – 0.01% of Ca, Mg, Al, Si, and Sn were prepared by pouring together the solution which is 1% with respect to platinum and appropriate amounts of 0.0002, 0.0006, 0.002, 0.006, and 0.02% solutions of the salts of the impurities being determined. The solutions prepared in this way contained 0.5% Pt and 0.0001, 0.0003, 0.001, 0.003, and 0.01% of the impurities being determined.

The calibration curves prepared (Fig. 1) permitted determination of down to 0.002% of Ca, down to 0.02% of Mg, 0.02% of Al and Si, and 0.06% Sn. The mean error for the determination of calcium, magnesium, and aluminum was ±6%, while the error for determination of silicon and tin was ±9%.

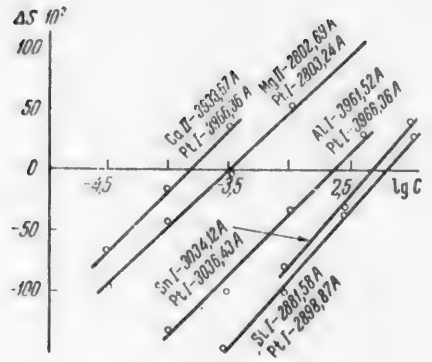

Fig. 1

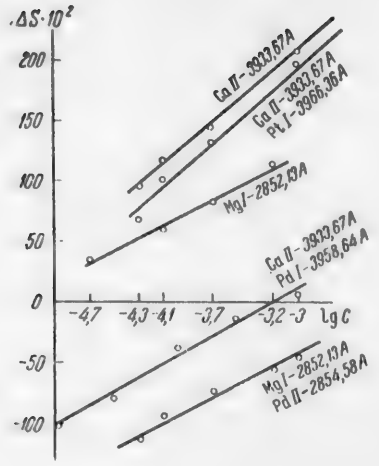

Fig. 2

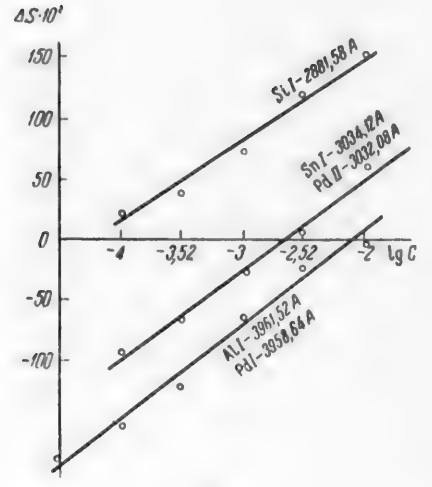

Fig. 3

The calcium content of the original platinum was found by extrapolation to be 0.002%.

Standard solutions for the determination of Ca, Mg, Al, Si, and Sn in refined palladium were prepared in the same way as for platinum. The original palladium contained 0.003% each of calcium and magnesium. After purifying the palladium by means of palladozammine the content of these impurities was lowered to 0.0012% for calcium, and 0.0005% for magnesium. Nevertheless, even after five reprecipitations of palladium as $(NH_3)_2Cl_2Pd$ the calcium and magnesium contents did not decrease.

The palladozammine which had been reprecipitated several times (up to five times) was then reduced in a stream of hydrogen; 6, 2, and 1% solutions were then prepared from the palladium formed, for this purpose the aliquots of palladium were dissolved in aqua regia (both the hydrochloric and nitric acids were redistilled beforehand in quartz vessels).

The nitric acid was then removed by careful boiling with concentrated hydrochloric acid. As the nitrogen oxides were removed the solution was diluted with water and then evaporated to minimum volume, the solution was transferred to a standard flask and made up to the mark with water.

The content of calcium, magnesium, aluminum, and tin in the standard solution prepared was varied from 0.2 to 0.006%, and that of silicon from 0.1 to 0.0003% with respect to the palladium. The palladium concentrations of the solutions were 0.5 and 1%.

The solutions were poured into the sprayer and sprayed in the course of three minutes into the arc between carbon electrodes, the interelectrode distance being 3 mm; fresh solution was passed into the sprayer every minute. The reference line was that of palladium; in addition, the background near the analytical line was also used.

In the case of the 1% solution of palladium which gave very intense lines differing strongly from the analytical line of the test element, platinum was added as an internal standard, the concentration of the platinum being 0.1%.

The background was photographed in those cases where the lines of the internal standard were either far from the analytical line of the test element, or where they possessed incommensurable intensity. Calibration curves obtained by making photometric measurements on the basis of the background, and those obtained on the basis of the lines of platinum or palladium as reference lines, had the same slope to the concentration axis. (Figs. 2 and 3).

The analytical lines used were:

Ca	II	3933.67	Pd	I	3958.64
			Pd	I	3922.96
Mg	I	2852.13	Pd	II	2854.58
Al	I	3961.52	Pd	I	3958.64
Sn	I	3034.12	Pd	II	3032.08
Si	I	2881.58			background

The accuracy of determination when the spectra of the same solution was photographed several times on the same plate, or on another plate of the same type was not less than 6-7%.

The sensitivity for determinations in platinum and palladium solutions amounted to: $1 \cdot 10^{-5}$ % Ca, $3 \cdot 10^{-5}$ % Mg, $1 \cdot 10^{-4}$ % Al, $1 \cdot 10^{-4}$ % Si, $3 \cdot 10^{-4}$ % Sn.

The original palladium was found by the extrapolation method to contain 0.001% Ca and 0.0005% Mg.

SUMMARY

A method has been developed for the spectrographic determination of calcium, magnesium, aluminum, silicon, and tin in refined platinum and palladium, in which the metals are brought into solution beforehand. Recommendations are given for the preparation of reference solutions.

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QUANTITATIVE DETERMINATION OF FLUORIDE BASED ON FORMATION OF HYDROXYTRIFLUOROBORATES

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The formation and hydrolysis of fluoroborate complexes has been studied in detail by Ryss and co-workers [1]. They showed that on mixing hydrofluoric and boric acids, there occurs almost immediate formation of hydroxyfluoroboric acid:

$$3HF + H_3BO_3 = HBF_3OH + 2H_2O \quad (1)$$

Hydroxyfluoroboric acid HBF_3OH is a strong acid which dissociates to give H^+ and BF_3OH^- ions.

At the same time formation of tetrafluoroborates occurs in solution:

$$HF + HBF_3OH = HBF_4 + H_2O. \quad (2)$$

Reaction (2) is significantly slower than reaction (1) and is catalyzed by H^+ ions.

Formation of BF_3OH^- ions in solution is given as an explanation by I. G. Ryss for the impossibility of carrying out an accurate alkalimetric determination of HBF_4.

Taking into account the high rate of reaction (1) and the low rate of reaction (2), particularly at low hydrogen ion concentrations, we tried to develop a method for the quantitative determination of F^-, based on the alkalimetric titration of the borax formed according to the reaction:

$$3NaF + 5H_3BO_3 = NaBF_3OH + Na_2B_4O_7 + 7H_2O. \quad (3)$$

Solutions with a known concentration of fluoride were prepared by dissolving accurately weighed aliquots of sodium fluoride in twice-distilled water.

The sodium fluoride was prepared from chemically pure recrystallized sodium carbonate and 40% hydrofluoric acid. The latter was prepared by diluting liquid hydrogen fluoride with twice-distilled water in a platinum basin.

The liquid hydrogen fluoride contained not more than 0.173% H_2SiF_6, 0.013% SO_4^{2-}, 0.141% SO_2, heavy metals 0.004%, and nonvolatile residue 0.0085%.

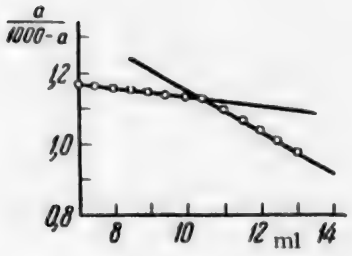
The sodium fluoride was prepared by adding sodium carbonate to the 40% hydrofluoric acid in such amount that 95% of the acid was neutralized. The solution was evaporated slightly and the precipitated NaF filtered, the NaF was then recrystallized and calcined at 400°.

The crystals showed a neutral reaction to phenolphthalein. In order to control the purity of the product thus obtained, aliquots of the crystals were treated three times in a platinum basin with redistilled, chemically pure hydrochloric acid, after each hydrochloric acid treatment the mass was evaporated to dryness; the product

obtained was calcined at about 600° and weighed. The following results were obtained: 0.1672 and 0.7914 g of NaF yielded 0.2341 and 1.1022 g of NaCl; the theoretical amounts of NaCl were 0.2329 and 1.1023 g.

An aliquot of sodium fluoride was dissolved in 30% boric acid solution and the solution obtained titrated conductometrically with hydrochloric acid.

The setup used for conductometric titration consisted of a ZG-4 sonic generator, a drum rheocord, and a resistance box. The null instrument was a four tube a.c. null indicator. Measurements were carried out at a frequency of 1000 cycles.



Conductometric titration curve.

A glass vessel with fused-in platinized platinum electrodes was used. The vessel constant was 0.8622 cm^{-1}. The experimental results are given in Table 1.

From the diagram it is evident that the end point can be determined quite clearly; in all cases, however, the results obtained were 2-5% low (see Table 1).

The low results obtained can be explained by the hydrolysis of $NaBF_3OH$ with formation of borofluoride complexes with a lower fluorine content. In order to prevent hydrolysis, in subsequent analyses the solution was diluted with an equal volume of ethanol. Results of these determinations are given in Table 2.

As the results given in Table 2 show, titration of solutions containing up to 0.1 g of fluoride can be carried out with an accuracy of ±0.3%. For lower fluoride contents the error increases slightly, and, at fluoride contents of 0.02 – 0.04 g of fluoride, it amounts to ±0.8%.

TABLE 1

Determination of Fluoride as $NaBF_3OH$ in Aqueous Solutions

F taken, in g	F found, in g	Relative error, in %
0,0190	0,0186	−2,1
0,0190	0,0182	−4,2
0,0190	0,0183	−3,7
0,0474	0,0464	−2,1
0,0950	0,0924	−2,7
0,1900	0,1820	−4,2
0,0950	0,0904	−4,8

TABLE 2

Determination of Fluoride in Aqueous-Alcoholic Solution as $NaBF_3OH$

F taken, in g	F found, in g	Relative error, in %
0,2488	0,2483	−0,20
0,1967	0,1970	+0,15
0,1893	0,1892	−0,05
0,1727	0,1732	+0,29
0,1516	0,1518	+0,13
0,0917	0,0916	−0,11
0,0650	0,0653	+0,46
0,0394	0,0391	−0,76
0,0206	0,0207	+0,48
0,0463	0,0465	−0,43

Taking into account the possibility that reaction (2) occurs, in some cases, conductometric titrations were carried out 24 hours after mixing. The analytical results obtained under these conditions were the same as those obtained previously. The effect of various anions on the accuracy of fluorine determination was also studied.

As the results given in Table 3 show, strong acid anions (SO_4^{2-}, NO_3^-, Cl^-) present as impurities, increase the relative experimental error to 1%.

In the presence of considerably larger amounts of these impurities the relative error increases to 4%.

Weak acid anions interfere with the determination. Presumably, all cations which give precipitates at a pH of 7.5 should interfere with fluorine determination by this method.

In view of the interest in determining the fluoride content of heavy metal fluorides, the technique described was used for determining fluoride in cobalt, manganese, and antimony fluorides.

TABLE 3

Effect of Various Anions on the Accuracy of Fluoride Determination

Impurity	Ratio of NaF: impurity (g/mole)	Weight of F taken, in g	F found, in g	Relative error, in%
NaCl	1:9	0.1423	0.1366	−4
NaCl	1:1.5	0.1900	0.1903	+0.16
NaCl	1:1	0.2014	0.2025	+0.54
Na_2SO_4	3:1	0.0385	0.0383	−0.52
Na_2SO_4	1:10	0.1908	–	–•
$NaNO_3$ + +NaCl + $+Na_2SO_4$	1:1	0.2185	0.2165	−0.92••
$NaNO_3$ + +NaCl + $+Na_2SO_4$	1:1	0.1818	0.1835	−0.93••

•A precipitate formed on addition of alcohol.

••Equal amounts (in g-mole) of NaCl, Na_2SO_4, and $NaNO_3$ taken.

TABLE 4

Determination of Fluoride in Co, Mn, and Sb Salts

Test mixture	Fluoride taken, in g	Fluoride found in g	Relative error, in %
$Co(NO_3)_2$	0.1393	0.1400	+0.50
$Co(NO_3)_2$	0.1371	0.1384	+0.95
$Co(NO_3)_2$	0.1477	0.1485	+0.55
$MnCl_2$	0.1362	0.1350	−0.88
$MnCl_2$	0.1384	0.1386	+0.14
$SbCl_3$	0.1363	0.1358	−0.37
$SbCl_3$	0.1394	0.1409	+1.08
$SbCl_5$	0.1814	0.1803	−0.61
$SbCl_5$	0.1519	0.1534	+0.98

In view of the difficulty of preparing the fluorides of the metals indicated, with a known fluoride content, we determined fluoride in mixtures of sodium fluoride with the equivalent amounts of $Co(NO_3)_2$, $MnCl_2$, $SbCl_3$, and $SbCl_5$.

Analytical procedure. An accurately weighed aliquot of sodium fluoride was mixed with an aliquot of one of the salts indicated. The mixture was treated with an appropriate amount of 1 N NaOH, taken in an excess of 1.5 and 2 with respect to the mixture, and the whole boiled for one hour. The alkali treatment was carried out in 250 ml stoppered conical flask. The stopper was fitted with two tubes for passage of oxygen purified from CO_2, and with a dropping funnel for adding water, when necessary, to the flask. The precipitate was filtered through a fine filter and then washed with hot water until the total volume of filtrate obtained was 250 ml (the filtrate and wash liquors were collected in a 250 ml standard flask); 50 ml of this solution was transferred to the titration flask, where it was neutralized with 0.1 N hydrochloric acid using phenolphthalein as indicator; 1.2 g of boric acid was added, followed by 50-60 ml of distilled ethanol, and, after cooling to room temperature, the solution was titrated conductometrically with 0.1 N HCl.

As the results given in Table 4 show, the relative experimental error for determination of fluoride does not exceed 1.1%. When the test material does not contain Co, Mn, Sb etc., the alkali treatment is not given.

SUMMARY

A method has been developed for the quantitative determination of fluoride which is based on conductometric titration of the borax formed during the reaction: $3NaF + 5H_3BO_3 = NaBF_3OH + Na_2B_4O_7 + 7H_2O$.

The method has been applied to the determination of fluoride in cobalt, manganese, and antimony fluorides.

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•Original Russian pagination. See C. B. Translation.

NEW COLOR REACTIONS FOR FERRICYANIDES

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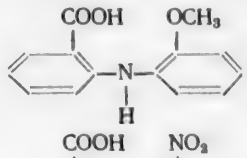
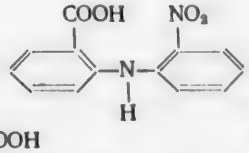
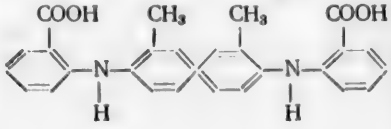
Despite the fact that in recent years a fairly large number of color reactions have been suggested for the ferricyanide ion, very few photometric methods are known for its determination. This is a consequence of the fact that the final reaction product is, in most cases, a precipitate which may have different colors. Almost all the known reactions for ferricyanides are based on the capacity of the latter to oxidize certain organic materials (benzidene, p-phenetidine, o-toluidine, and α-naphthylamine [1], dimethyl- and diethylanilines [2], dimethylaminoantipyrine and tetramethyldiaminodiphenylmethane [3]) to form brightly colored reaction products. The sensitivity of such reactions can be increased considerably by removing the ferricyanide ions from the reaction sphere by precipitation with zinc ions. Further, reagents which are organic bases are often precipitated by ferricyanides. In the absence of zinc ions the reaction has a low sensitivity.

All the reactions mentioned are not very specific, since similar reactions are given in an acid medium by most strong oxidizing agents.

TABLE 1

Sensitivity of Certain Diphenylaminecarboxylic Acids Toward the Ferricyanide Ion

Acid	Formula	Color of the reaction product	Sensitivity, γ/ml
o'-Methoxyphenylanthranilic acid		Red	23,0
o'-Nitrophenylanthranilic acid		Brown-yellow	1,0
Diphenylbenzidene-o,o'-dicarboxylic acid		Red-brown	2,3
Diphenyltolidine-o,o'-dicarboxylic acid		Brown-red	0,5

Willard and Monalo [4] have shown that certain substituted diphenylaminecarboxylic acids are capable of being oxidized by ferricyanides in alkaline media to form colored products. These reactions are highly specific

TABLE 2

Molar Extinction Coefficients of the Reagents Studied

V_{total}, in ml	$V_{reagent}$, in ml	$C_{original}$, in moles	Molar conc. of the oxidation product	ϵ	ϵ molar
For diphenyltolidine-o,o'-dicarboxylic acid					
5	0,34	10^{-3}	$0,68 \cdot 10^{-4}$	1,23	$3,63 \cdot 10^4$
10	0,34	10^{-3}	$0,34 \cdot 10^{-4}$	0,66	$3,59 \cdot 10^4$
10	0,68	10^{-3}	$0,68 \cdot 10^{-4}$	1,23	$3,63 \cdot 10^4$
				Average	$3,62 \cdot 10^4$
For o'-nitrophenylanthranilic acid					
4	0,33	10^{-3}	$0,63 \cdot 10^{-4}$	0,21	$0,67 \cdot 10^4$
4	1,00	10^{-3}	$2,5 \cdot 10^{-4}$	0,62	$0,64 \cdot 10^4$
				Average	$0,65 \cdot 10^4$

TABLE 3

Determination of Potassium Ferricyanide in Potassium Ferrocyanide by Means of Diphenyltolidene-o,o'-dicarboxylic Acid

Taken, in γ	Found, in γ	Taken, in γ	Found, in γ
30	28	3.0	3.2
65	66	12.0	11.4
90	90	8.5	8.5

for ferricyanides (in alkaline media almost all known strong oxidizing agents do not oxidize diphenylamine derivatives).

We have studied the sensitivity of the detection of ferricyanide ions in a medium of 5 N NaOH by a spot technique using the following diphenylaminecarboxylic acids: phenylanthranilic, and meta-N-phenylaminobenzoic acids, o,o'-diphenylaminedicarboxylic acid and its meta- and para isomers, the three isomeric tolylanthranilic acids, o-methoxyphenylanthranilic, o'- and para'-nitrophenylanthranilic acids, and diphenylbenzidene-o,o'-dicarboxylic acid. The most sensitive reagents are given in Table 1. The sensitivity of the diphenylaminecarboxylic acids toward ferricyanide ions drops rapidly with increasing alkali concentration (starting at 1 N and higher). The sensitivity of the reaction with o-nitrophenylanthranilic acid starts to drop even in a medium of 0.3 N sodium hydroxide. Accordingly, for this acid, the sensitivity was determined in a medium of 0.1 N sodium hydroxide.

The reagents studied form, with potassium ferricyanide in alkali solution, red-brown solutions with a maximum light absorption at 470 mμ (Fig. 1). The reaction takes 3-4 minutes to go to completion.

The results obtained during a study of the system "reagent–ferricyanide ion" by the Ostromyslenskii-Job-Babko method are shown in Figs. 2 and 3; they show that diphenylamine derivatives in alkali media are oxidized according to a scheme similar to that for their oxidation in acid media; two equivalents of the oxidizing agents are used up for oxidizing the organic molecule.

The molar extinction coefficients of oxidized solutions of o'-nitrophenylanthranilic and diphenyltolidine-o,o'-dicarboxylic acids are given in Table 2. During calculation it was assumed that the molar concentration of the colored reaction product formed is equal to the molar concentration of the acid taken for oxidation.

The oxidation products of o-nitrophenylanthranilic and diphenyl tolidenedicarboxylic acids conform to the Lambert–Beer law over a certain range of concentration (for the first acid over the range 10-100 γ in 5 ml, and for the second acid over the range 30-300 γ in 4 ml).

Preponderant amounts of ferricyanides do not interfere with the reaction.

Photometric determination of traces of ferricyanide in potassium ferrocyanide is carried out as follows: to 0.1-1.0 ml of test solution containing not more than 100 γ / ml of ferricyanide ion, and contained in a test

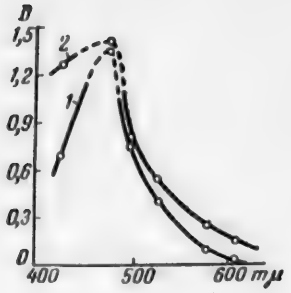


Fig. 1. Light absorption curves of the oxidized products of o-nitrophenylanthranilic acid (I) and diphenylbenzidene-o,o'-dicarboxylic acid (II).

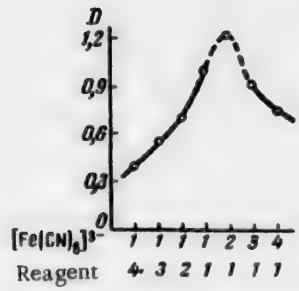


Fig. 2. The system ferricyanide–diphenyltolidene-o,o'-dicarboxylic acid (V_{total} – 5 ml; $C_{original}$ – 10^{-3} M; λ – 480 mμ; d – 5 mm; 0.05 N KOH.

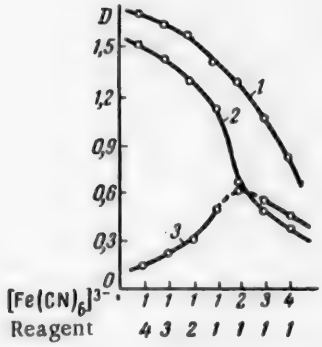


Fig. 3. The system ferricyanide–o-nitrophenylanthranilic acid: V_{total} – 4 ml; V – 3 ml; $C_{original}$ – 10^{-3} M; λ – 480 mμ; d – 5 mm; 0.05 N KOH; I) reagent–reaction product; II) reagent; III) reaction product.

tube is added 0.2 ml of a 0.1% solution of the reagent (o-nitrophenylanthranilic or diphenyltolidene-o,o'-dicarboxylic acid) in a 0.1% solution of sodium carbonate. After mixing, the contents of the test tube are made up to a volume of 5 ml with 0.05 N sodium or potassium hydroxide. The solutions are left for 5 minutes after which photometric measurements are made at 470 mμ in a cell with a layer thickness of 5 mm. Water is used as the compensating liquid. A calibration curve can be constructed by means of a solution of recrystallized potassium ferricyanide [5]. Some idea of the accuracy of the method is given in Table 3.

Synthesis of reagents. o-Nitrophenylanthranilic acid was synthesized according to Ullmann's method [6]. Diphenyltolidene-o,o'-dicarboxylic acid* was synthesized in similar fashion to diphenylbenzidene-o,o'-dicarboxylic acid [7]. The synthesis was carried out as follows: a mixture of 3 g of o-chlorobenzoic acid, 2 g of o-tolidene, 2.7 g of potassium carbonate, and 20 ml of isoamyl alcohol was heated to the boil for 2 hours in the presence of a small amount of "naturkupfer C." Excess isoamyl alcohol was removed by steam distillation, after which the reaction product was precipitated by means of 1 : 1 hydrochloric acid. The acid obtained was filtered on a Buchner funnel and dried at 110°. 2.75 g of crude was obtained, this was purified by dissolving it in a 0.1% solution of sodium carbonate, and was again precipitated with dilute hydrochloric acid. Diphenyltolidene-o,o'-dicarboxylic acid is a powdery material with a dark-green color, and has a rather ill-defined melting point at about 300°. The following results were obtained during a nitrogen determination:

Calculated for $C_{28}H_{24}O_4N_2$, nitrogen 6.19%.

Found for $C_{28}H_{24}O_4N_2$, nitrogen 6.03%.

SUMMARY

The new color reactions are described for the ferricyanide ion; photometric methods of determining potassium ferricyanide in the presence of large amounts of potassium ferrocyanide have been developed on the basis of these reactions.

*We are the first to prepare this reagent.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF WATER OF CRYSTALLIZATION IN CERTAIN CRYSTALLOHYDRATES ON THE BASIS OF THEIR ABSORPTION SPECTRA IN THE NEAR INFRARED (0.8 – 2.5 μ)

D. S. Gorbenko-Germanov, R. A. Zenkova and T. L. Bolotina

The present article contains a description of a method for the quantitative determination of water of crystallization on the basis of the infrared absorption spectra in the 0.8 – 2.5 μ region of crystallohydrates in the solid phase. Milligram amounts of test material are necessary in order to get reliable results by this method.

The spectrum of liquid water in the region 0.8 – 2.5 μ [1-2]. In order to choose an analytical band for subsequent investigation of crystallohydrates, absorption spectra were taken in the 0.8 – 2.5 μ region for a layer thickness of 0.046 – 100 mm. All measurements were carried out on a IKS-11 infra-red spectrometer.

In Fig. 1 is shown the absorption spectrum of water in the 0.8 – 2.5 μ region.

The band H_2O_{liquid} 5130 cm^{-1} was chosen as the analytical band on the basis of the following considerations:

1. The band at 5130 cm^{-1} has the greatest intensity.

2. At wavelengths shorter than 1.9 μ there was observed a continuous absorption, determined by the low transparency of the solid preparations in the wavelength shorter than 1.9 μ.

The technique used for taking spectra of preparations in the solid phase. Some modifications were made to the standard IKS-11 model, since the apparatus as it stood did not ensure the necessary accuracy of measurement.

a) The recorder used was one taken from a MF-4 microphotometer which had a more accurate recording scale (1000 mm long with 1 mm divisions) and permitted the spectra to be photographed on a plate.

b) More accurate apparatus was used for controlling the heating current in the FEOU-15 amplifier (a millivoltmeter with a scale of 17 millivolts and an universal M-16 measuring apparatus were used).

c) For more accurate deciphering of the spectra, the datum lamp was provided with an additional button, by means of which it was possible to direct vertical datum lines onto the spectrograms for an arbitrary reading of the wavelength drum.

d) So that it should be possible to photograph the spectra of dense samples, the FEOU-15 amplifier was operated in its high range (tube 2.5 volts, 0.55 amp. at a voltage of 2.4 volt).

In order to take photographs of the absorption spectra of samples in a solid state, the technique of pressing in an optically inactive diluent was used (calcined, ground potassium chloride, which is transparent up to 20 μ). The mixtures, containing varying amounts of the crystallohydrate were pressed into tablets in a hydraulic press. At a pressure of 220-230 kilos / cm^2, and for a diameter of the press-form of 12 mm, and 117 mg of test mixture, tablets with a thickness of 0.55 ± 0.01 mm were obtained. The tablet thickness was measured to an accuracy of 0.01 mm with a micrometer.

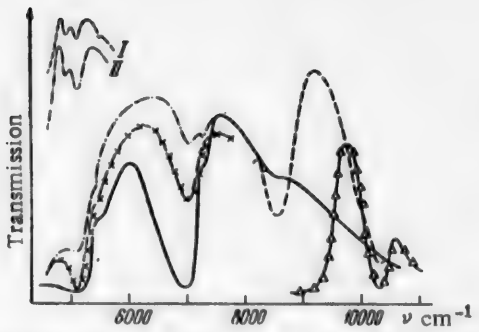

Fig. 1. Absorption spectra of H_2O_{liquid} in the 5000-11000 cm^{-1} region.
I and II) absorption spectra of $Eu_2(SO_4)_3 \cdot 8H_2O$ —·—·— 0.74% water, tablet thickness 1.23 mm; – – – – – 0.4% water, tablet thickness 1.49 mm. Cell thickness: — — — 1 mm; —·—·— 0.046 mm; -x-x-x 0.200 mm; – – – – 10 mm; -Δ-Δ-Δ- 100 mm.

When photographs were taken of the absorption spectra of various crystallohydrates it was found that the band at 5130 cm^{-1} in the crystallohydrates, in a number of cases, suffers a shift of 100-200 cm^{-1}.

In Fig. 1 (Curves 1 and 2) and in Fig. 2 is shown the absorption band at 5130 cm^{-1} for various crystallohydrates.

The construction of a calibration curve, and the method of calculating optical density at extreme points. The standard chosen for constructing the calibration curve was the octahydrate of europium sulfate $Eu_2(SO_4)_3 \cdot 8H_2O$; the latter was chosen for the following reasons:

1) This crystallohydrate is highly stable;

2) It is possible to control the stability of this compound during the process of taking the infrared absorption spectra, on the basis of the nature of the splitting of the electronic bands of Eu^{3+} which is observed in the 4000-5500 A region (a sharp quintet in the 4600 A region and a sharp triplet in the 5200 A region [3]). Control was realized by means of a ISP-51 spectrograph with a camera with F = 800 mm.

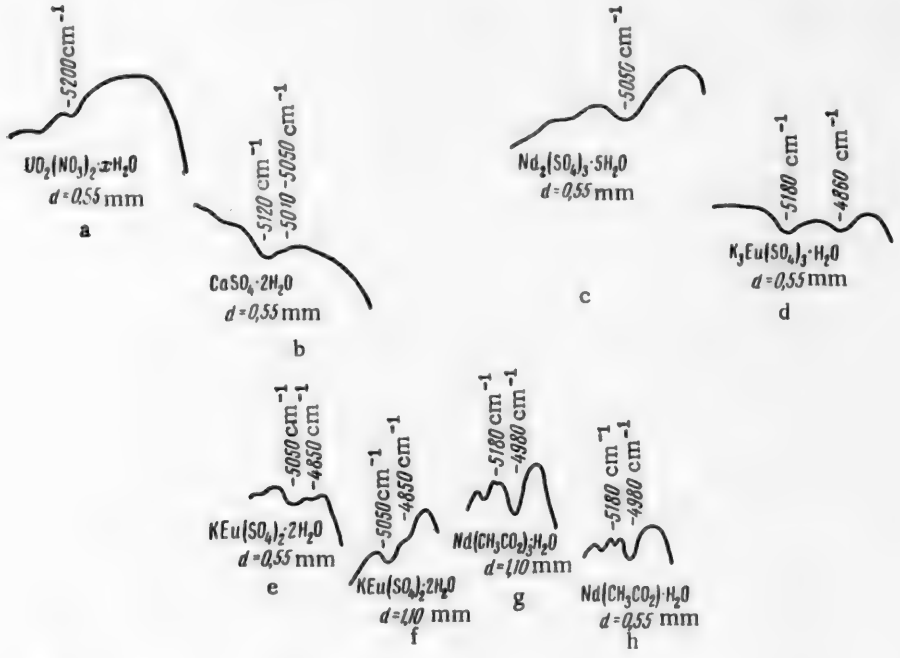

Fig. 2. The band H_2O_{liquid} 5130 cm^{-1} in certain crystallohydrates:
a) $UO_2(NO_3)_2 \cdot H_2O$ (d = 0.55 mm); b) $CaSO_4 \cdot 2H_2O$ (d = 0.55 mm); c) $Nd_2(SO_4)_3 \cdot 5H_2O$ (d = 0.55 mm); d) $K_3Eu(SO_4)_3 \cdot H_2O$ (d = 0.55 mm); e) $KEu(SO_4)_2 \cdot 2H_2O$ (d = 0.55 mm); f) $KEu(SO_4)_2 \cdot 2H_2O$ (d = 1.10 mm); g) $Nd(CH_3COO)_3 \cdot H_2O$ (d = 1.10 mm); h) $Nd(CH_3COO)_3 \cdot H_2O$ (d = 0.55 mm).

In order to construct a calibration curve within the coordinates optical density and water content, amounts of europium sulfate octahydrate varying from 0.5 to 21.1 mg were used for making tablets with a weight of 117 mg (0.078 – 3.52% of water or 0.09 – 4.12 mg of water in a tablet).

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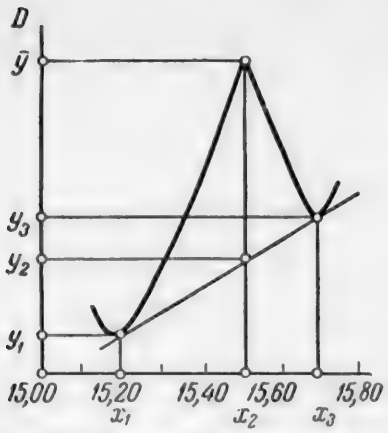


Relative divisions of the wavelength drum of the monochromator

Fig. 3. Calculation of the optical density at the extreme points.

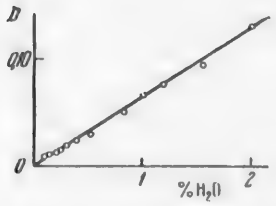


Fig. 4. Calibration curve.

In order to determine the position of the three extreme points corresponding to the maximum transmission of the tablets on both sides of the absorption maximum (x_1 and x_3), and the point of maximum absorption (x_2) (Fig. 3), a qualitative photograph of the spectra was taken using additional datum lines. Subsequently, measurements were only made at these three points; when a switch was made to another crystallohydrate for which a shift in the absorption band was observed, a qualitative photograph was again taken and the extremal points x_1, x_2, and x_3 determined and measurements then carried out only at these three points.

For calculating the value of $\bar{y} - y_2$ it is possible to use the general form of the equation for a straight line

$$y = Ax + B \qquad (1)$$

For the points x_1, x_2, and x_3 it is possible to write three equations:

$$y_1 = Ax_1 + B; \qquad (2)$$
$$y_2 = Ax_2 + B; \qquad (3)$$
$$y_3 = Ax_3 + B. \qquad (4)$$

By removing A and B from (2) and (4) and substituting their values in (3) we get:

$$y_2 = \frac{x_2(y_1 - y_3) + x_1y_3 - x_3y_1}{x_1 - x_3} \qquad (5)$$

In the case of $Eu_2(SO_4)_3 \cdot H_2O$, the points x_1, x_2, and x_3 had the values 15.20, 15.52, and 15.70 respectively (relative divisions of the wavelength drum).

Substituting these values in (5) and simplifying, we get:

$$y_2 = 0.36y_1 + 0.64\ y_3 \qquad (6)$$

or the value of D at the absorption maximum is given by

$$D = \bar{y} - y_2 = \bar{y} - 0.64\ d_1 - 0.36\ d_2, \qquad (7)$$

where d_1 and d_2 are the optical densities at points x_3 and x_1 respectively, while $\underline{y}$ is the optical density at the maximum absorption band.

In the case of another crystallohydrate, new values of x_1, x_2, and x_3 are substituted in (5) and a new equation derived.

Determinations were carried out by measuring the transmission of tablets containing the crystallohydrates at the extreme points, and then the transmission of potassium chloride tablets was measured immediately at the same points.

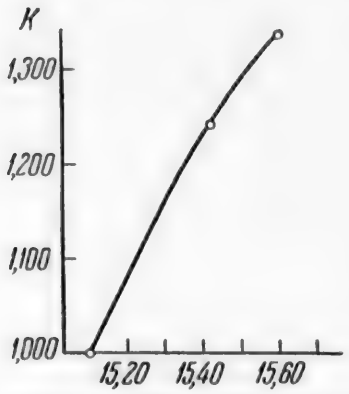
The optical density was calculated by the well-known equation

$$D = \log \frac{I_0}{I} = K_\nu cd, \qquad (8)$$

where I_0 and I are the transmissions of tablets of potassium chloride and of tablets containing the crystallohydrates respectively.

Results obtained by this method are presented graphically in Fig. 4.

It was observed that potassium chloride tablets measured at different times had different transmissions at the extreme points, while the ratio of the transmissions at these points kept approximately constant. This fact permitted the determination of the mean ratios of the transmissions for the background of the tablets at the extreme points (point x_1 being taken as unity), and helped us to calculated the value of the background at points x_2 and x_3 (the transmission of the test sample, and the value of the background at point x_1, were equal to one another). Under these conditions the third member on the right hand side of equation (7) became zero.



Relative divisions of the wavelength drum of the monochromator

Fig. 5. Relation between the mean values of the background and the relative divisions of the wavelength drum of the monochromator.

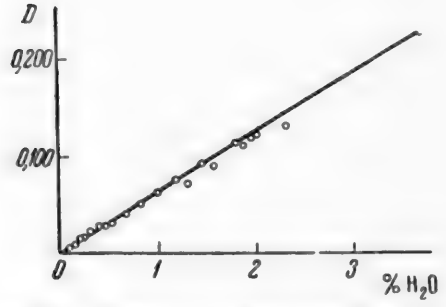


Fig. 6. The calibration curve for the method of the mean values of the background at the extreme points.

Using this method all former test samples prepared at various times and photographed for various slit widths of the monochromator were recalculated. The calibration curve obtained is shown in Fig. 6.

The simplicity of the calculation, the short time taken to make measurements, and also the small relative error in the determination of the optical density enabled us to determined the amount of water of crystallization in various crystallohydrates.

The Quantitative Determination of the Water of Crystallization of Certain Crystallohydrates

1) Double sulfates of potassium and europium. For the system $K_2SO_4 - Eu_2(SO_4)_3 - H_2O$ we identified the following individual compounds: $KEu(SO_4)_2 \cdot H_2O$ (1), $KEu(SO_4)_2 \cdot 2H_2O$ (2), $K_3Eu(SO_4)_3 \cdot H_2O$ (3).

For compounds (1) and (2) the position of the extreme points coincided with that found for europium sulfate octahydrate, and the calculation was made according to the equation $D = \bar{y} - 0.64\, d_1$.

In the case of compound (3), the points x_1, x_2, and x_3 had the following values: 15.20, 15.64, and 15.75 and calculations were made according to the equation: $D = y - 0.80\, d_1$.

Fifteen samples (from 7.22 to 23.13 mg of compound in a tablet) were taken for analysis of (1); the mean value amounted to 4.6% of water (theoretical water content – 4.49%; 5.3% by gravimetric analysis).

For the analysis of (2), 12 samples were taken (from 8.58 to 17.64 mg of compound in a tablet); mean value 7.4% water (theoretical water content 8.59%; 8.7% by gravimetric analysis).

Four samples (from 24.97 to 38.50 mg in a tablet) were taken for the analysis of (3); mean value, 2.8% of water (theoretical water content 3.13%; by gravimetric analysis 3.0%).

The results obtained confirm the composition of compounds (1), (2), and (3).

2. Neodymium sulfate. Calculations were made on the basis of $D = \bar{y} - 0.64\, d_1$; the position of the extreme points coincided with that found for europium sulfate octahydrate $Eu_2(SO_4)_3 \cdot 8H_2O$. Nine samples, 6.28 mg per tablet were taken for analysis; the mean value found was 12.4% (theoretical water content calculated on the basis of the formula $Nd_2(SO_4)_3 \cdot 5H_2O$ 13.51%); by gravimetric analysis 10.0%.

These results confirm the composition $Nd_2(SO_4)_3 \cdot 5H_2O$.

3. Neodymium acetate. The experimental points x_1, x_2, and x_3 for this compound had the values 15.22, 15.48, and 15.62; calculations were made on the basis of the equation $D = \overline{y} - 0.65\, d_1$. Six samples containing from 12.8 to 28.5 mg of the compound per tablet were taken; the average value found for the water was 5.2% (the theoretical water content based on the formula $Nd(CH_3COO)_3 \cdot H_2O$ is 5.3%). The compound was not analyzed gravimetrically.

4. Calcium sulfate. The experimental points x_1, x_2, and x_3 for this compound were 15.42, 15.58, and 15.75; calculations were made on the basis of the euqation $D = \overline{y} - 0.33\, d_1$. Three samples each containing 6.56 g of the compound per tablet, were taken for analysis; the mean value found for water was 19.0% (the theoretical water content based on a formula of $CaSO_4 \cdot 2H_2O$ is 20.9%; the value found gravimetrically was 20.6%). The results obtained confirm the formula $CaSO_4 \cdot 2H_2O$.

This method permits determination of micro amounts of water in samples, the weight of which would not allow reliable gravimetric determination. The amount of test material in which it would still be possible to determine the water content reliably, can be decreased a few times more by using tablets with a smaller diameter and thickness.

SUMMARY

1. The absorption spectrum of H_2O_{liquid} in the 0.8-2.5μ region has been studied. The H_2O_{liquid} band at 5130 cm^{-1} is displaced by 100-200 cm^{-1} in crystallohydrates, and, in some cases, splits up. The shift and the splitting of the band at 5130 cm^{-1} testifies to a fairly deep penetration of the water molecules into the crystallohydrate molecule.

2. Calibration curves have been obtained and methods of calculating optical density at three extreme points are suggested. A method is described for the determination of water of crystallization in crystallohydrates.

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NEW METHODS FOR THE QUANTITATIVE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS

II. GRAVIMETRIC DETERMINATION OF CHLORINE, BROMINE, AND IODINE

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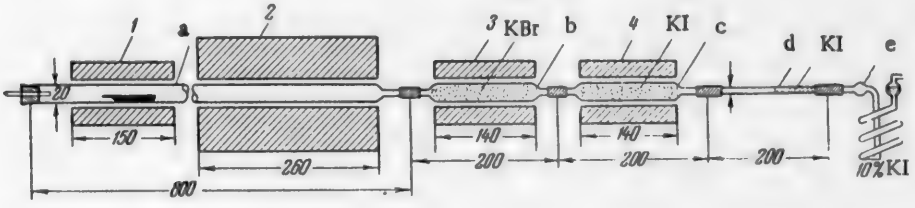
The S. O. Makarov Nikolaev Shipbuilding Institute

All published methods for the quantitative determination of chlorine, bromine, and iodine can be divided into two main groups – gravimetric and volumetric. All the gravimetric methods are based on combining the halogen with silver and then weighing the silver halides.

In our first communication [1] we described new quantitative volumetric methods of determining chlorine, bromine, and iodine in organic materials. In the present article a description is given of new gravimetric methods for the quantitative determination of each of the elements indicated, which do not involve the use of silver.

The new gravimetric methods of determining the halogens are based on differences in their chemical activity. The organic compound is broken down by one of the published methods, for example, by combustion in an atmosphere of oxygen or in air. The gaseous reaction products, containing the free halogens, and the hydrogen halides, are passed through two heated tubes filled in succession with metal bromides (see diagram). In the first tube b bromine ions are oxidized by the free chlorine, while in the second tube c iodine ions are oxidized by the liberated bromine. In the third tube d, filled with moist potassium iodide, the liberated iodine is trapped quantitatively. A Winkler apparatus is connected to tube d, this apparatus being filled with a solution of 10% potassium iodide for trapping traces of iodine carried through by the oxygen stream. The chlorine and bromine contents of the test sample are then calculated on the basis of the changes in weight of tubes b and c. The iodine content of the test sample is calculated from the difference between the total amount of iodine condensed in tube d and trapped by the Winkler apparatus, and the amount of chlorine and bromine found from the changes in weight of tubes b and c. In this way it is possible to determine chlorine, bromine, and iodine separately on one aliquot of test material. Methods for the quantitative determination of two and three halogens on one aliquot of test material will be described in a future article.



EXPERIMENTAL

a) Quantitative determination of chlorine. The apparatus is assembled (see diagram). Tube d is moistened with water; it is then dipped in a bottle of potassium iodide and 2-3 g of this compound introduced into it, care being taken to ensure that the potassium iodide is not too closely packed so as to hold up the passage of the gases

TABLE 1

Gravimetric Determination of Halogens

Test material	Weight of sample in g	Decrease in tube wt. g	% Halogen			Tube filled with:
			calc.	found	difference	
Hexachloroethane	0,1104	0,1244	89,89	89,86	−0,03	KBr
"	0,0742	0,0836	89,89	89,85	−0,04	KBr
"	0,0956	0,1078	89,89	89,92	+0,03	NaBr
"	0,1174	0,1322	89,89	89,80	−0,09	NaBr
"	0,1338	0,3102	89,89	89,87	−0,02	KI
Polyvinylchloride	0,0921	0,1350	56,73	56,82	+0,09	KI
Dibromobenzene	0,0722	0,0288	67,76	67,81	+0,05	KI
"	0,0562	0,0224	67,76	67,74	−0,02	KI

through it. 5-8 ml of a 10% solution of potassium iodide is poured into the Winkler apparatus. The first oven is heated to 750-800°, while the second is heated to 800-900°, an the third and fourth heated to 650-680° and 450-500° respectively. The temperature of the third and fourth ovens is measured by means of thermocouples.

Purified and dried oxygen is passed at the rate of 150-200 ml/minute for 15-20 minutes through the apparatus with the ovens switched on. The absorption apparatus is then disconnected. The tubes filled with bromide and iodide are sealed with rubber caps and transferred to the balance room, where they are allowed to cool (30-40 minutes), they are next weighed and reconnected to the apparatus. Test material is weighed out into a boat, and powdered quartz sand or chromium oxide strewn over it. When chromium oxide is used [2] combustion proceeds better, but this oxide cannot be used repeatedly because of loss in activity. The boat and sample are placed in the combustion tube at a distance of 2-3 cm from the point at which the tube enters the first oven. By gradually shifting the oven [1] the sample is set alight or is evaporated. The vapors from the material and its decomposition products pass with the oxygen stream into the calcining zone, where its complete breakdown occurs. This process takes 10 to 30 minutes depending on the nature of the test material. Finally the tube is heated strongly along the whole of its length for another 5-10 minutes. The absorption apparatus is disconnected again and tubes b and c covered with the rubber caps; they are removed to the balance room, and after 30-40 minutes weighed (without the rubber caps). The contents of tube d and of the Winkler apparatus are transferred quantitatively by washing into a flask in which the solution is titrated with 0.05 N sodium thiosulfate. For evaporating the material and heating the tubes filled with potassium bromide and iodide, it is expedient to use hinged ovens.

Calculation of the chlorine content (in %) can be carried out as follows:

1. From the change in weight of tube b containing potassium (sodium) bromide.

2. From the change in weight of tube c containing potassium iodide.

3. From the weight of iodine condensed in tube d and the Winkler apparatus.

If desirable one can manage with one tube, for example, one filled with potassium bromide b, or potassium iodide c, or with tube d filled with moist potassium iodide, and the Winkler apparatus. In the last instance, determination is carried out volumetrically [1]. The chlorine content is calculated by means of the following formulas:

1. From the change in weight of tube b containing potassium bromide

$$\% \mathrm{Cl} = \frac{\mathrm{Cl} \cdot b_1 \cdot 100}{a\,(\mathrm{Br} - \mathrm{Cl})};$$

where Cl is the gram-equivalent of chlorine; b_1 is the decrease in weight of the tube containing potassium bromide; a is the weight of test material.

2. From the change in weight of tube c containing potassium iodide

TABLE 2

Gravimetric and Volumetric Determination of Halogens

Test material	Wt. of sample, in g	Change in sample wt. containing: KBr, in g	KI, in g	0.05 N $Na_2S_2O_3$ used for titration, ml	%Halogen from calculations based on KBr			%Halogen	from calculations based on KI		%Halogen	from calculations based on I	
					calc.	found	difference	calc.	found	difference	calc.	found	difference
Hexachloroethane	0.0727	0,0820	0,0866	36,84	89,89	89,95	+0,06	89,89	89,85	−0,04	89,89	89,83	−0,06
Dichlorobenzene	0.0388	0,0234	0,0249	10,56	48,23	48,09	+0,14	48,23	48,40	+0,17	48,23	48,25	+0,02
Bromocamphor	0,0 16	—	0,0145	6,20	—	—	—	34,57	34,43	−0,14	34,57	34,60	+0,03
Dibromobenzene	0,0614	—	0,0245	10,40	—	—	—	67,76	67,84	+0,09	67,76	67,68	−0,08

$$\%\,Cl = \frac{Cl \cdot b_2 \cdot 100}{a\,(I - Cl)};$$

where Cl is the gram-equivalent of chlorine; b_2 is the decrease in weight of tube c containing potassium iodide; a is the weight of test material; I − Cl is the difference between the atomic weights of iodine and chlorine.

3. From the amount of iodine liberated

$$\%\ Cl = \frac{Cl \cdot k \cdot 100}{20000 \cdot a},$$

where Cl is the gram-equivalent of chlorine; k is the volume of 0.05 N sodium thiosulfate used in ml; a is the weight of test material.

b) Quantitative determination of bromine. The analysis is carried out in the apparatus shown in the diagram, the tube containing potassium bromide is omitted, however.

The bromine content (in %) is calculated: 1. From the change in weight of the tube c containing potassium iodide:

$$\%\,Br = \frac{Br \cdot b_2 \cdot 100}{(I - Br) \cdot a};$$

where Br is the gram-equivalent of bromine; b_2 is the decrease in weight of tube c containing potassium iodide; a is the weight of test material.

2. From the amount of iodine collected in tube d and the Winkler apparatus, and subsequently titrated with sodium thiosulfate

$$\%\ Br = \frac{Br \cdot k \cdot 100}{20000 \cdot a};$$

where Br is the gram-equivalent of bromine, k is the volume of 0.05 N sodium thiosulfate used, in ml; for titrating the liberated iodine; a is the weight of test material.

c) Quantitative determination of iodine. Determination of iodine is carried out in the same way as that indicated for chlorine and bromine, in this case, however, the tube c containing iodide, and tube b with bromide are not included in the apparatus. The contents of tube d and the Winkler apparatus are quantitatively washed into a flask and the iodine titrated with 0.05 N sodium thiosulfate.

The iodine content is calculated by means of the formula:

$$\%\,I = \frac{I \cdot k \cdot 100}{20000 \cdot a},$$

where I is the gram-equivalent of iodine; k is the volume of 0.05 N sodium thiosulfate; a is the weight of test material.

Tables 1 and 2 contain some results illustrating the applicability of the method.

SUMMARY

A new gravimetric (and volumetric) method has been developed for determining chlorine, bromine, and iodine in organic materials, one element at a time; the method is based on differences in the activity of the halogens. The method is simple, and does not require complicated apparatus, expensive reagents, or silver – which is normally employed – or complicated techniques.

Experimental error does not exceed ± 0.1 – 0.2%. An analysis takes 40-50 min. The accuracy of the value obtained for chlorine can be checked in three ways during the determination, while the value for bromine can be checked in two ways. Sulfur interferes with determination of the halogens.

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*Original Russian pagination. See C. B. Translation.

DETERMINATION OF CYCLOHEXANONE AND CYCLOHEXANOL IN EACH OTHERS PRESENCE

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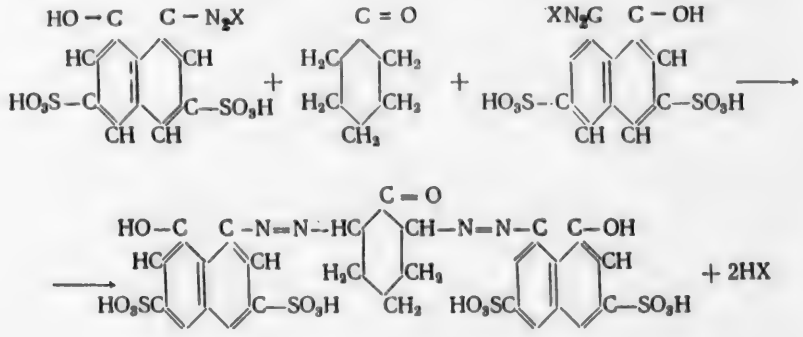
Cyclohexanone and cyclohexanol find wide application as solvents for many organic materials, and as intermediate products in industrial organic synthesis. Methods of determining cyclohexanone and cyclohexanol based on the reactions of their functional groups [1, 2] are complicated to carry out and take a long time; they are normally carried out in a nonaqueous medium and are only applicable to high concentrations. Other methods are based on condensation and polymerization reactions [3, 4, 5] and are only applicable for the determination of each taken separately, or for one in the presence of insignificant amounts of the other.

We have developed a convenient method for the determination of cyclohexanone and cyclohexanol in each others presence. Determination of cyclohexanone is based on its reaction with the diazonium salt of H-acid (1-naphthylamine-8-hydroxy- 3,6-disulfonic acid). We were the first to establish the capacity of cyclohexanone to couple with the diazonium salt of H-acid to form a cherry-red dye according to the equation:



The reaction sensitivity is 0.2 γ/ml. We prepared the azo dye in a pure state and established its composition. The color of solutions obtained during the reaction of cyclohexanone with the diazonium salt of H-acid conforms to the Beer law (Fig. 1). Maximum light absorption is observed at 550 mμ (Fig. 2).

The molar extinction coefficient is 15700.

The diazonium salt of H-acid possesses a sharply expressed capacity to undergo a self coupling reaction in which intensely colored products with a blue color are formed. This fact complicates the use of H-acid in photometric analysis as the diazo component. The addition of sodium sulfite or bisulfite to the test solution, however, prevents this self coupling of diazotized H-acid.

During determination of cyclohexanone in the presence of cyclohexanol, a small amount of the latter is oxidized to cyclohexanone, a factor which leads to slightly high results for cyclohexanone. The addition of acetic anhydride and urotropine (hexamethylenetetramine) prevents this process. Metabisulfite, acetic anhydride, and urotropine do not affect the coupling of the diazonium salt of H-acid with cyclohexanone.

Cyclohexanol was determined on the basis of the reaction with diphenylamine. On heating a solution of cyclohexanol in the presence of diphenylamine in a sulfuric acid medium at temperatures higher than 100°, a red color develops. The composition of the colored compound has not been established. The color of the solution does not conform to Beer's law (Fig. 1). Maximum light absorption is observed at 530 mμ (Fig. 2). The reaction sensitivity is 5 γ/ml.

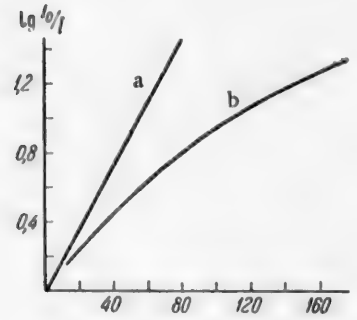


Fig. 1. Conformation of solutions to Beer's law:
a) Relation between optical density and cyclohexanone concentration during its reaction with the diazonium salt of H-acid; b) ditto for cyclohexanol during its reaction with diphenylamine.

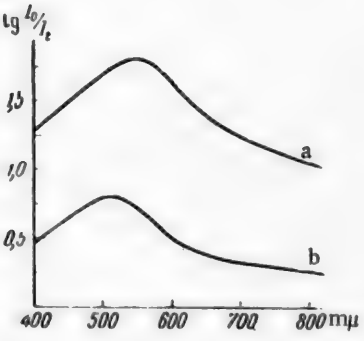


Fig. 2. Absorption curves:
a) Light absorption by solutions obtained during the reaction of cyclohexanone with the diazonium salt of H-acid. Cyclohexanone concentration 10 γ/ml; b) ditto for cyclohexanol during its reaction with diphenylamine. Cyclohexanol concentration 25 γ/ml of solution.

Cyclohexanone in amounts up to 0.5 mg/ml does not give a color with diphenylamine on heating in a sulfuric acid solution. Higher concentrations of cyclohexanone give weak colors. Addition of hydroxylamine sulfate to the solution prevents formation of a color in the presence of cyclohexanone. The addition of hydroxylamine sulfate to the test solution does not have any appreciable effect on the reaction between cyclohexanol and diphenylamine.

Determination of Cyclohexanone

Reagents. 1. A standard aqueous solution of cyclohexanone containing 40 γ/ml.

2. A freshly prepared solution of diazotized H-acid. This is prepared by mixing equal volumes of a 1% solution of sodium nitrite, and a 0.25% solution of the mono-sodium salt of H-acid in 0.05 N sulfuric acid.

3. Acetic anhydride.

4. A 10% solution of urotropine.

5. A freshly prepared 1% solution of sodium metabisulfite.

6. A 25% solution of sodium hydroxide.

Analytical procedure. To 1 ml of test solution contained in a colorimeter tube is added 0.2 ml of urotropine solution and a drop (0.02 ml) of acetic anhydride. After mixing, 0.2 ml of the sodium metabisulfite solution and 0.2 ml of the sodium hydroxide solution are added, followed by 0.5 ml of the diazo salt of H-acid. After 5 minutes the solution is diluted accurately to the mark with water and the color intensity measured. A calibration curve for use in the photocolorimetric determination of cyclohexanone is constructed by taking various amounts of the standard solution of cyclohexanone in a series of colorimeter tubes. After the volumes in the tubes have been made equal by addition of water, the reagents are added, the volumes made up to 10 ml with water, and the color intensity measured on a photocolorimeter using a green filter.

Cyclohexanone can also be determined on the basis of its reaction with the diazonium salt of H-acid by the technique of colorimetric titration with a standard aqueous solution of the azo dye. In this case, into the control sample, after it has been diluted with water to 10 ml, is added dropwise from a microburet, a standard aqueous solution of the azo dye, until the color is the same as that of the test solution; the cyclohexanone content of the sample is then calculated from the amount of the azo solution added. 7.58 γ of azo dye is equivalent to 0.98 γ of cyclohexanone.

The azo dye required for the preparation of the standard solution to be used for the determination of cyclohexanone by colorimetric titration can be prepared by the procedure given below. To 100 ml of a 2% suspension of the mono-sodium salt of H-acid in 0.1 N hydrochloric or sulfuric acid is added dropwise 5 ml of a 10% solution of sodium

TABLE 1

Determination of Cyclohexanone in the Presence of Cyclohexanol by means of the Reaction with the Diazonium Salt of H-Acid

Taken		Cyclohexanone found, γ	Error, %
cyclohexanone, γ	cyclohexanol, mg		
1,0	—	1,09	+9,0
2,0	0,2	1,94	−3,0
—	0,3	0,00	0,0
4,0	0,3	3,75	−6,2
5,0	0,5	5,25	+5,0
7,0	0,5	7,6	+8,5
8,0	0,6	8,2	+2,5
10,0	1,0	9,65	−3,5
12,0	1,0	12,6	+5,0
15,0	1,5	14,7	−2 0
18,0	1,5	17,5	−2,7
20,0	2,0	21,2	+6,0
22,0	2,0	22,8	+3,6
25,0	2,5	24,2	−3,2
28,0	2,5	28,0	0,0
30,0	3,0	31,3	+4,3
32,0	3,0	32,4	+1,2
34,0	3,5	33,6	−1,1
35,0	3,5	37,0	+5,7
40,0	4,0	39,5	−1,3

TABLE 2

Determination of Cyclohexanol in the Presence of Cyclohexanone by means of the Reaction with Diphenylamine

Taken		Cyclohexanol found, in γ	Error, in %
cyclohexanol, in γ	cyclohexanone in mg		
10,0	0,10	11,2	+12,0
15,0	0,20	13,4	−10,6
20,0	0,30	18,4	− 8,0
—	0,50	0,0	− 0,0
25,0	0,50	26,2	+ 4,8
30,0	0,80	28,1	− 6,3
—	1,0	0,0	0,0
35,0	1,0	36,3	+ 3,7
40,0	1,0	38,2	− 4,5
45,0	1,5	41,5	− 8,7
50,0	1,5	53,5	+ 7,0
55,0	1,5	54,2	− 1,4
60,0	1,5	56,4	− 6,0
65,0	2,0	69,3	+ 6,6
—	2,0	0,0	0,0
70,0	2,0	66,1	− 5,6
75,0	2,0	78,8	+ 4,6
80,0	—	85,0	+ 6,3
90,0	2,0	92,8	+ 3,1
100	2,5	97,8	− 2,2

nitrite. The suspension of the H-acid, after addition of sodium nitrite, at first dissolves, but a yellow precipitate of the diazonium salt then separates out. After 5 minutes, 500 mg of cyclohexanone and 25 ml of an alkali mixture consisting of equal parts of 20% solutions of sodium sulfite and sodium hydroxide, are added to the reaction mixture. After addition of the alkali mixture, the precipitate of diazonium salt and H-acid dissolves, and the solution acquires an intense cherry-red color. After 20 minutes, 50% sulfuric acid is added dropwise to the solution until the color changes from cherry-red to brown, and until a precipitate is formed. Solution and precipitate are transferred to a No. 3 sintered funnel on which the solution is sucked off; the precipitate is washed three times with alcohol and dried in a drying oven at 105°. The yield is about 2 g.

Results of determinations of cyclohexanone in the presence of cyclohexanol are given in Table 1.

Determination of Cyclohexanol

Reagents: 1. A standard aqueous solution of cyclohexanol containing 100 γ / ml.

2. A 2% solution of diphenylamine in concentrated sulfuric acid.

3. A 25% aqueous solution of hydroxylamine sulfate.

Analytical procedure. To 2 ml of the test solution of cyclohexanol contained in a colorimeter tube is added 2 ml of the solution of diphenylamine in sulfuric acid. A standard scale is prepared at the same time. For the latter purpose various amounts of the standard solution of cyclohexanol, ranging from 10 to 100 γ, are introduced into a series of colorimeter tubes. When the volume in each tube has been adjusted to 2 ml, 2 ml of the diphenylamine solution is added to each of them. When the cyclohexanone content of the test material has been found to be greater than 1 mg, then 0.2 ml of the hydroxylamine sulfate solution is also added to each of the tubes. The colorimeter tubes forming the scale, and the tube containing test solution, are placed for 15 minutes in an oil bath kept at a temperature of 145-150°. After 15 minutes, the tubes are removed from the oil bath, wiped with cotton wool or paper, and the color intensity measured. Results for the determination of cyclohexanol by the reaction with diphenylamine are given in Table 2.

For the determination of cyclohexanone and cyclohexanol in air, water can be used as the sorbent. The air to be tested is drawn through three wash bottles, connected in series; each bottle contains water, and the

and the air is drawn through them for one hour at the rate of 15-20 liters per hour. At the end of this time, 1 ml of liquid is taken from each wash bottle for determination of cyclohexanone, and 2 ml for the determination of cyclohexanol; analysis is then carried out by the methods described above. Usually, 70-80% of the cyclohexanone and about 90% of the cyclohexanol is trapped in the first wash bottle; in the second 20-30% of cyclohexanone, and about 10% of cyclohexanol is trapped. There is only a very insignificant break-through of cyclohexanone into the third wash bottle, when the concentration of cyclohexanone in air is higher than 20 γ/liter.

SUMMARY

A photometric method has been developed for the determination of cyclohexanone which is based on its reaction with the diazonium salt of H-acid; this technique permits determination of cyclohexanone in the presence of 100 times its amount of cyclohexanol. The sensitivity of the method is 0.2 γ/ml. Experimental error does not exceed 9% for cyclohexanone concentrations within the limits 1 to 40 γ in the test material.

A method has been developed for the determination of cyclohexanol by means of diphenylamine, which permits determination of cyclohexanol in the presence of 30 times its amount of cyclohexanone. The experimental error over the range 10 to 100 γ does not exceed 12%. The sensitivity of the method is 5 γ/ml.

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DETERMINATION OF PRIMARY, SECONDARY, AND TERTIARY AMINO GROUPS IN EACH OTHERS PRESENCE

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During a study of the nitrogenous compounds found in petroleum we developed a method for the determination of primary, secondary, and tertiary amino groups in each others presence. This method can be successfully applied to the analysis of mixtures of aliphatic and aromatic amines. The methods most widely used for the determination of primary amino groups are those of Van-Slyke, and diazometric titration with sodium nitrite of a solution of an aromatic amine in a strong mineral acid medium. One of the essential drawbacks of these methods is their inapplicability to the analysis of mixtures containing secondary amino groups. Tertiary amino groups can be determined in the presence of primary and secondary amino groups, when the primary and secondary amino groups are either destroyed beforehand by HNO_2 [1-2], or are acetylated by acetic anhydride [3].

In 1947 Wagner, Brown, and Peters [4] suggested an acidimetric method for the separate determination of primary, secondary, and tertiary aliphatic amino groups in each others presence. A little later, Siggia, Hanna, and Kewenski [5] extended this method to mixtures of aromatic amines.

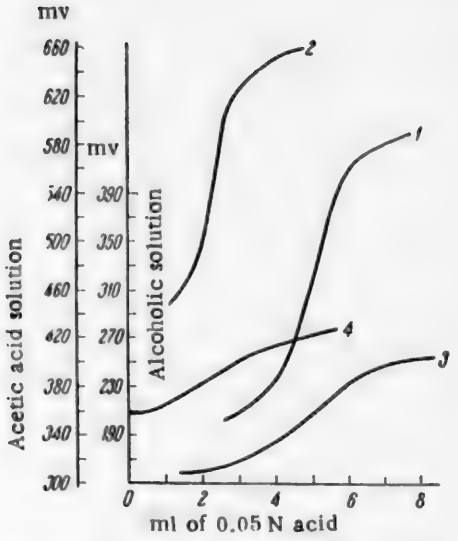
Their method consists of the following stages: first the total amino group content in the mixture is determined; in a second aliquot, the primary amino groups are then blocked by combination with salicylaldehyde $RNH_2 + OHC \cdot C_6H_4OH \rightarrow RN = CH \cdot C_6H_4OH + H_2O$. The Schiff bases which are thereby formed are weak bases which do not interfere with total acidimetric titration of secondary and tertiary amino groups. In a third aliquot of the sample the primary and secondary amino groups are acetylated with acetic anhydride, and the tertiary amino group, which remains unchanged, is then titrated. Knowing the total amino group content, the sum of the secondary and tertiary amino groups, and the tertiary amino content, it is easy to calculate the content of primary and secondary amino groups.

In the papers cited, the amino groups were determined either by titration in the presence of an indicator, or by potentiometric titration. The solvents used were isopropanol [4], and a mixture of isopropanol and ethylene glycol [5]; the titrants used were solutions of $HClO_4$ or HCl in the same solvents. The essential drawback of this method is the difficulty associated with determining the endpoint, arising from the fact that the alcohols used by the authors as solvents (isopropanol and ethylene glycol) are differentiating solvents with weakly expressed protogenic properties. Accordingly, the strength of the bases in these alcohols is only insignificantly higher than that in aqueous solutions. In practice, it is only possible to titrate those bases whose ionization constants are not less than $10^{-7} - 10^{-8}$.

After treatment of the mixture with salicylaldehyde the sensitivity of the reaction is lowered further, since salicylaldehyde always contains salicylic acid as an impurity, and this interferes with the titration.

Furthermore, the Schiff bases formed are titratable – though only to a small extent – in alcoholic solution.

In recent years, it has been shown in a series of papers [6-8], that glacial acetic acid is the best solvent for the acidimetric titration of amines. Amines are titrated very distinctly in a medium of glacial acetic acid. Amines whose ionization constants are of the order of $10^{-11} - 10^{-12}$ can be titrated in this solvent.



Titration curves for mixture IV (Table 2). 1) Titration of the mixture with $HClO_4$ in CH_3COOH; 2) titration of the mixture with $HClO_4$ after preliminary treatment with salicylaldehyde; 3) titration of mixture with HCl in isopropanol – ethylene glycol; 4) titration of the mixture with HCl after preliminary treatment with salicylaldehyde.

Nevertheless, the Schiff bases formed during the interaction of primary amines with salicylaldehyde are equal in strength to secondary and tertiary amines. As a result, during titration in glacial acetic acid of a mixture of amines containing Schiff bases, and secondary and tertiary amines, the total of amino groups is determined. The potentiometric titration curve in such cases has only one break.

In order to make it possible to carry out a differential determination of primary, secondary, and tertiary amino groups in a glacial acetic acid medium, we used phthalic anhydride instead of salicylaldehyde for quantitative blocking of the primary amino groups. Phthalic anhydride reacts with primary amines in glacial acetic acid to form the corresponding phthalimides. The latter, under the given conditions, behave as neutral substances, and, in contrast to the Schiff bases, do not interfere at all with subsequent titration of secondary and tertiary amines. The suitability of phthalic anhydride for the quantitative blocking of primary amino groups has been checked on a number of individual amines, and on mixtures of amines containing, in addition to primary amino groups, secondary and tertiary amino groups (Tables 1 and 2).

The results we obtained showed that phthalic anhydride can be successfully used for the quantitative blocking of primary amino groups in the presence of secondary and tertiary amino groups. The definition and accuracy of titration of the residual secondary and tertiary amino groups does not suffer at all under these conditions; the potential jump at the endpoint has almost the same value as for a solution of amines in glacial acetic acid in the absence of phthalimides.

Potentiometric titration curves are shown in the diagram for titration of mixture IV (Table 2), after treatment of this mixture with salicylaldehyde (Curve 4), and with phthalic anhydride (Curve 2). While the potential jump in the case of titration of amines in an alcoholic medium only amounts to 30-40 millivolts, in a glacial acetic acid medium this jump is 70-100 millivolts, i.e., the sensitivity of potentiometric titration more than doubles. As the results given in Tables 1 and 2 show, the method suggested proved to be fully suitable for the quantitative determination of primary amino groups in a number of aliphatic amines (determinations 1-6), aromatic amines (determinations 7-12), and for 3-aminopyridine and 3-aminoquinoline. The absolute experimental error, as a rule, is not more than 0.1% for a nitrogen content greater than 10%.

It should be pointed out that in the series pyridine, quinoline, and thiazole, the amino group in positions 2 and 4 possesses properties which are more amide-like than amino. During titration of 2- and 4-aminopyridines and aminoquinolines in glacial acetic acid with $HClO_4$, it is the monoperchlorates not the diperchlorates that are formed. Amino groups located in positions 2 and 4 do not react with either phthalic anhydride or acetic anhydride, and, accordingly, cannot be determined by this method. 2-Aminothiazole behaves in the same way. The amino group located in position 3 in the pyridine and quinoline ring reacts with phthalic anhydride, and can be titrated with $HClO_4$ in glacial acetic acid, i.e., it possesses basic properties. Thus, where 2- and 4-aminopyridines and quinolines are present in a mixture, the primary amino groups in these compounds cannot be determined by the method suggested (determinations 13, 14, 16, and 18 in Table 1). Tertiary amines were determined in the presence of primary and secondary amines by blocking the latter with acetic anhydride and titrating the residual tertiary amine in solution [9].

Experimental Procedure. Redistilled glacial acetic acid was used as the solvent.

Titration was carried out using 0.05 or 0.1 N $HClO_4$ in glacial acetic acid. The standard acid solution

TABLE 1

Acidimetric Determination of Primary Amines in Glacial Acetic Acid by Means of Phthalic Anhydride

Expt. No.	Test compound	Calculated, in %				N Found, in %	
		N_{total}	NH_2	NH	N	N_{total}	N after treatment with phthalic anhydride
1	Butylamine	19.15	19.15	–	–	19.23	0
						19.17	0
2	Amylamine	16.07	16.07	–	–	16.15	0
						16.15	
3	Isopropylamine	23.70	23.70	–	–	23.50	0
						23.51	
4	Di-n-amylamine	8.91	–	8.91	–	8.80	8.80
						8.85	8.88
5	Di-n-butylamine	10.84	–	10.84	–	10.74	10.77
						10.63	10.70
6	Methyloctadecylamine	4.94	–	4.94	–	5.01	4.95
						5.04	–
7	Aniline	15.05	15.05	–	–	15.07	0
						15.01	0
8	p-Toluidine	13.07	13.07	–	–	13.07	0
						13.07	0
9	o-Toluidine	13.07	13.07	–	–	12.98	0
						13.05	0
10	p-Anisidine	11.38	11.38	–	–	11.42	0
						11.42	0
11	p-Aminophenol	11.19	11.19	–	–	11.14	0
						11.13	0
12	n,n',p,p'-Diaminodiphenyl-disulfide	11.28	11.28	–	–	11.33	0
						11.35	0
13	2-Aminopyridine	29.77	14.88	–	14.88	14.76	14.82
						14.80	14.83
14	4-Aminopyridine	29.77	14.88	–	14.88	14.68	14.65
						14.65	14.60
15	3-Aminopyridine	29.77	14.88	–	14.88	29.52	14.70
						29.62	14.65
16	2-Aminoquinoline	19.43	9.71	–	9.71	9.63	9.72
						9.68	9.63
17	6-Methoxy-3-amino-quinoline	14.72	7.36	–	7.36	14.62	7.38
						14.65	7.34
18	2-Aminothiazole	27.97	13.98	–	13.98	13.90	13.92
						13.81	13.93

was prepared from aqueous $HClO_4$ (40 or 70%) and glacial acetic acid, the water introduced being removed by addition of the calculated amount of acetic anhydride. The normality of this solution was established by titrating against a solution of potassium hydrogen phthalate in glacial acetic acid. Perchloric acid can be replaced by p-toluenesulfonic acid, which, in glacial acetic acid, behaves like a very strong acid [10]. It is essential to ensure that the temperature of the titrant does not change during titration. A LP-5 tube potentiometer was used for carrying out potentiometric titration. Titration was carried out with the aid of a glass stirrer connected to an electric motor.

An aliquot of test sample, the amount taken being dependent on the nitrogen content, is transferred to a

TABLE 2

Acidimetric Determination of Primary, Secondary, and Tertiary Amino Groups in Mixtures of Amines by Means of Phthalic Anhydride

No. of mixture	Amine mixture	Weight of sample in 100 ml of solution	Amount HCl used for titrating 25 ml of solution, ml			Calculated, in %				Found, in %			
			$N_{original\ +\ total}$	total NH + N•	N••	N_{total}	NH_2	NH	N	N_{total}	NH_2	NH	N
1	Isopropylamine	0.1186	17.07	0	–	20.70	20.70	0	0	20.81	20.81	–	–
	Butylamine	0.0519	17.06	0	–					20.79	20.79	–	–
	Amylamine	0.0593											
2	Amylamine	0.0353	4.96	1.06	–	13.01	9.57	3.44	–	13.10	9.57	3.53	–
	Di-n-amyl-amine	0.0410	4.93	1.02	–					13.03	9.63	3.40	–
	Aniline	0.0297											
3	Aniline	0.0287	5.41	1.90	1.91	18.12	11.83•••	–	6.29	18.10	11.62	–	6.38
	p-Toluidine	0.0199	5.45	–	1.89					18.15	11.84	–	6.31
	2-Aminopyridine	0.0356											
4	Aniline	0.0489	5.03	2.36	0.92	13.67	7.18	3.84	2.65	13.75	7.29	3.95	2.51
	Methylanine	0.0301	5.05	2.33	0.97					13.80	7.41	3.73	2.66
	Dimethylaniline	0.0235											
5	Butylamine	0.0457	4.98	1.81	0.65	13.80	8.74	3.13	1.93	13.92	8.86	3.24	1.82
	Dibutylamine	0.0289	4.98	1.81	0.67					13.92	8.86	3.18	1.88
	Tributylamine	0.0255											

•After treatment of the solution with phthalic anhydride.

••After treatment of the solution with acetic anhydride.

•••Without taking into account the NH_2 group of 2-aminopyridine which is not titrated.

standard flask and made up to the mark with glacial acetic acid. An aliquot part of this solution (20-25 ml) is taken for each determination. Total amino nitrogen is determined on one part of the solution. To the second 20-25 ml lot of solution is added 1 g of phthalic anhydride (a two or threefold excess of the anhydride is taken with respect to the NH_2 groups); the solution is then heated under reflux on a boiling water bath for 30-45 minutes. The solution is cooled and the total secondary and tertiary amino groups remaining in solution determined by titration. To a third portion of solution is added 10-15 ml of acetic anhydride, and the mixture is heated under reflux on a boiling water bath for 30-45 minutes. The solution is cooled and the tertiary amino groups titrated. Knowing the total amino nitrogen, the sum of the secondary and tertiary amino groups, and the amount of tertiary amino groups, the content of primary and secondary amino nitrogen is calculated.

SUMMARY

A method is suggested for the acidimetric (potentiometric) determination of primary, secondary, and tertiary amino groups in a glacial acetic acid medium. The method is based on the quantitative blocking of primary amino groups with phthalic anhydride, and the blocking of primary and secondary amino groups with acetic anhydride. The use of acetic acid as solvent increases the potential jump at the end-point, and permits titration of nitrogen bases with dissociation constants of the order of $10^{-11} - 10^{-12}$.

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POLAROGRAPHIC DETERMINATION OF ALKYLNITRITES

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In recent years the problem of devising a reliable method for the quantitative determination of alkylnitrites (RONO) has become a real one. This is a consequence of the fact that according to modern concepts, alkylnitrites are formed as intermediates during nitration of paraffin hydrocarbons, probably according to the scheme:

$$\dot{R} + NO_2 \rightarrow RONO \qquad (1)$$

At the moment of its formation in this way the nitrite molecule, however, carries excess energy amounting to about 57 kilocalories/mole, since the energy of formation of the bond R – ONO is equal to this amount [1]. A nitrite molecule as rich in energy as this is characterized by extreme instability, since the dissociation energy of the adjacent bond RO–NO is only 37 kilocalories/molecule [2]. As a result it can be assumed that a nitrite molecule formed according to reaction (1), will immediately break down, and will give rise to the formation of an alkoxy radical and nitric oxide:

$$RONO \rightarrow \dot{RO} + NO. \qquad (2)$$

The alkoxy radical will undergo a series of further transformations, most of which will lead to the formation of oxygen-containing (without nitrogen) products, which are actually found during nitration of paraffins:

$$\dot{RO} \rightarrow R + HCHO; \qquad (3)$$

$$\dot{RO} + RH \rightarrow ROH + \dot{R}. \qquad (4)$$

In addition to reactions (3) and (4), the alkoxy radical can undergo one further transformation. As nitric oxide accumulates in the course of reaction (2) the probability of the reaction

$$RO + NO \rightarrow RONO, \qquad (5)$$

will increase; this reaction proceeds almost without any activation energy, since it is a recombination of two free radicals. Since the thermal effect of reaction (5) is 37 kilocalories/molecule [2], the nitrite molecule which is formed may be stable and remain without further decomposition.

Thus, if alkylnitrites are found in the nitration products of paraffins, these alkylnitrites should be regarded as products of secondary origin.

The polarographic method appeared to us to be the most promising method for the determination of the small amount of alkylnitrites found in the complex mixture of nitration products of paraffins, Bliumberg and Pikaeva [3] have found that ethylnitrite in aqueous solutions can be reduced electrolytically on a dropping mercury electrode at a half-wave potential of –0.96 volt; the latter is independent of the pH of the medium.

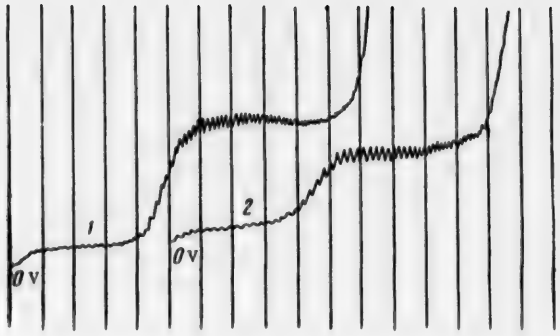

Fig. 1. Polarograms for ethyl- and butylnitrite in aqueous LiCl solutions:
1) Ethylnitrite in 0.1 N aqueous LiCl (ethylnitrite concentration 0.0386 wt. %); pH 2.5; 1 : 200; 20°; 2) butylnitrite in 0.1 N aqueous LiCl solution (butylnitrite concentration 0.013 wt. %); pH 2.9; 1 : 100; 20°.

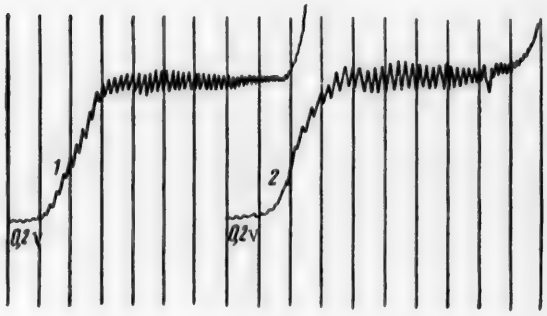

Fig. 2. Polarograms for ethyl- and butylnitrite in aqueous LiOH solutions.
1) Ethylnitrite in 0.1 N aqueous LiOH (ethylnitrite concentration 0.0284 wt. %); pH 12.2; 1 : 200; 20°; 2) butylnitrite in 0.1 N aqueous LiOH (butylnitrite concentration 0.09 wt. %); pH 12.3; 1 : 200; 20°.

These facts were used by the authors mentioned for the determination of ethylnitrite in the products formed by the interaction of ether with nitrogen peroxide in the gaseous phase [4].

We have also developed a polarographic method for the determination of alkylnitrites, taking ethylnitrite and butylnitrite as test materials.

The ethylnitrite was prepared by the action of concentrated hydrochloric acid on a mixture of an aqueous solution of $NaNO_2$ and ethanol [5]. The ethylnitrite thus prepared was dried over potassium hydroxide and distilled. The distilled product boiled at 17°.

Butylnitrite was prepared by pouring a mixture of sulfuric acid and butanol into an aqueous $NaNO_2$ solution [6]. After the mixture had separated into layers and the butylnitrite fraction had been removed, it was distilled under vacuum [24-27° (43 mm)]. The butylnitrite prepared had n_D^{20} 1.3770 (published value n_D^{20} 1.3773).

Solutions of the alkylnitrites prepared by dissolving aliquots of the nitrites, taken in glass ampoules, were subjected to polarographic study. In the case of ethylnitrite, the glass ampoule was cooled with solid carbon dioxide while it was being filled.

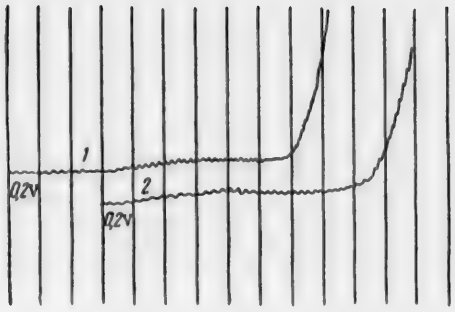

Fig. 3. Polarograms for aqueous solutions of ethyl- and butylnitrites in LiOH solutions: 1) An aqueous solution of ethylnitrite (ethylnitrite concentration 0.0574 wt. %) was mixed with an equal volume of 0.1 N aqueous LiOH; pH 11.8; 1 : 200; 20°; 2) an aqueous solution of butylnitrite (butylnitrite concentration 0.18 wt. %) was mixed with an equal volume of 0.1 N aqueous LiOH; pH 11.85; 1 : 200; 20°.

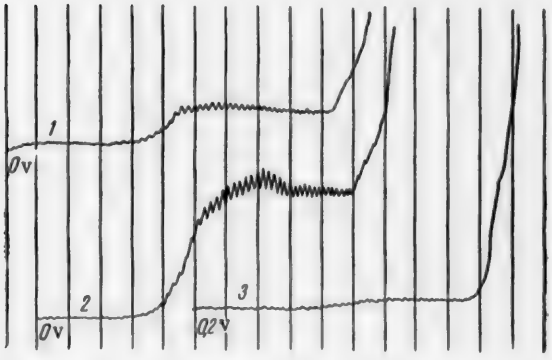

Fig. 4. Polarograms for aqueous $NaNO_2$ solutions at various pH values: 1) $NaNO_2$ in 0.1 N aqueous LiCl ($NaNO_2$ concentration 0.175 wt. %) plus 2 drops of HCl; pH 3.6; 1 : 500; 20°; 2) ditto plus another 2 drops of HCl; pH 3.0; 1 : 500; 20°; 3) ditto plus 0.2 N aqueous LiOH (1 : 1); pH 12.15; 1 : 200; 20°.

Oxygen dissolved in the electrolytes, was removed with a nitrogen stream before dissolving the alkylnitrites in them. Such a precaution is necessary because of the volatility of the alkylnitrites, particularly ethylnitrite.

Polarograms were taken on a polarograph made by the "Geologorazvedka" factory; the current–voltage curves were registered photographically.

The reduction potentials were measured relative to the saturated calomel electrode. The capillary used for making all measurements had the following characteristics $m^{2/3} t^{1/6} = 2.86\ mg^{2/3}\ sec^{-1/2}$; the pH of the solutions was measured on a LP-5 potentiometer with a glass electrode. The pH values adduced are uncorrected values.

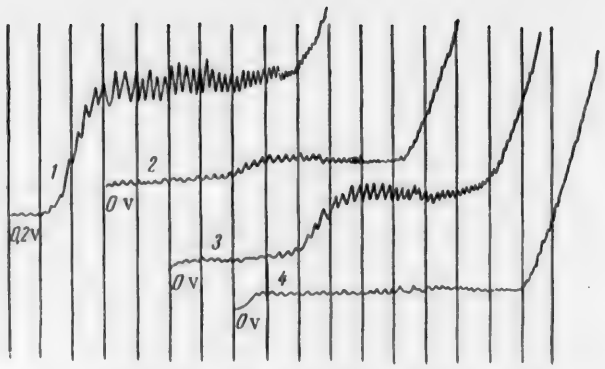

Fig. 5. Polarograms for butylnitrite in various media: 1) Butylnitrite in 0.1 N aqueous LiOH (butylnitrite concentration of 0.09 wt. %); pH 12.35; 1 : 200; 20°; 2) ditto plus HCl; pH 3.9; 1 : 200; 20°; 3) ditto plus some more HCl; pH 3.2; 1 : 200; 20°; 4) ditto plus concentrated LiOH solution; pH 12.35; 1 : 200; 20°.

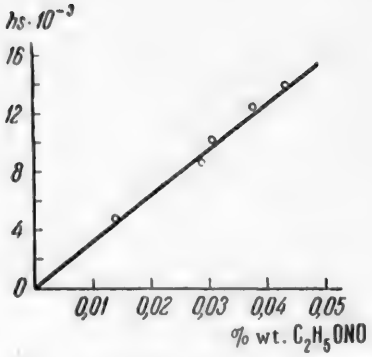

Fig. 6. Relation between the wave height for ethylnitrite and its concentrations in 0.1 N aqueous LiOH; pH 12.2; 20°.
h) wave-height, in mm; S) sensitivity.

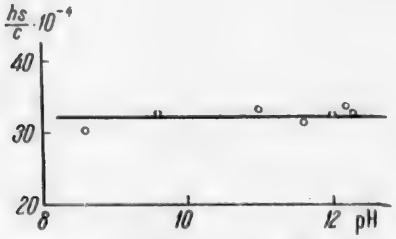

Fig. 7. Relation between the wave height of ethylnitrite and pH of the medium (LiCl + LiOH).
h) wave-height, in mm; S) sensitivity; c) concentration of ethylnitrite in wt. %.

Even the first experiments were sufficient to show that during polarographic determination of alkylnitrites is impossible to dissolve them in water or in aqueous solutions of electrolytes having a neutral or acid reaction. Under these conditions the alkylnitrites hydrolyze almost immediately to form alcohols and nitrous acid: $RONO + H_2O \rightarrow ROH + HNO_2$ (6). When this occurs there is a significant increase in the pH of the solution. For example, on dissolving $0.76 \cdot 10^{-3}$ g·mole of ethylnitrite in 100 ml of water, a solution with a pH of 2.7 was obtained, while on dissolving $1.02 \cdot 10^{-3}$ g·mole of ethylnitrite in 100 ml of a 0.1 N aqueous solution of LiCl a solution with a pH of 2.4 was obtained. The same was observed in the case of butylnitrite.

When polarograms were taken of solutions prepared in this way, there was observed quite a clear cut reduction wave for some compound at a half-wave potential of $\pi_{1/2} = -0.95$ volt. The only possible compound is nitrous acid, and, in fact, according to published results [7], the half-wave potential of this acid $\pi_{1/2} = -0.95$ volt (see also Curve 1, Fig. 4).

TABLE 1

Relation Between the Wave Height of Ethylnitrite and the Time it is in Contact with the Solution (LiOH)

Concentration of ethylnitrite in 0.1 N LiOH, in wt. %	pH of the solution	Wave height of ethylnitrite hS · 10^{-3}* when polarograms were taken after:				
		0 minutes	15 minutes	45 minutes	60 minutes	24 hours
0.04315	12.5	14	14	13	13	7
0.0356	8.6	10.8	10	9.8	9.4	–

*h) wave height, in mm; S) sensitivity.

Hydrolysis of alkylnitrites in aqueous alkali media is slowed down strongly. Actually, the pH of alkali solutions did not decrease on addition of alkylnitrites. Thus, on dissolving $0.6 \cdot 10^{-3}$ g-mole of ethylnitrite in 100 ml of 0.1 N aqueous LiOH (pH 12.2), the alkalinity of the solution obtained remained the same (pH 12.2). If the ethylnitrite had hydrolyzed, the pH of the solution would have been 11.9.

Ethylnitrite and butylnitrite dissolved in 0.2 or 0.1 N aqueous LiOH, are reduced at a half-wave potential of $\pi_{1/2} = -0.65$ volt (Fig. 2).

Final confirmation of the fact that taking polarograms of acid solutions of alkylnitrites is equivalent to electro-reduction of nitrous acid ($\pi_{1/2} = -0.95$ volt), and that electro-reduction of the alkylnitrites themselves is only possible in alkaline media ($\pi_{1/2} = -0.65$ volt), was obtained in subsequent experiments, the results of which are shown in Fig. 3.

It is shown in Fig. 3 that when alkylnitrites were dissolved in water (when this was done an acid solution was obtained which gave a wave for nitrous acid when polarograms were taken, see Fig. 1), and then mixed with LiOH, the solution became alkaline and then gave some other reduction wave (in addition to that for Li). Curve 3 in Fig. 4 shows that a nitrous acid solution which has been made alkaline does not give a reduction wave either.

Figure 5 demonstrates the behavior of butylnitrite in various media. Curve 1, Fig. 5 with a nitrite wave ($\pi_{1/2} = -0.65$ volt) was obtained when polarograms were taken of its alkaline solution in LiOH (pH 12.35). When this solution was acidified to a pH of 3.9 then, as is evident from Curve 2, the wave of the nitrite itself disappeared, since it hydrolyzed, and instead of it there appeared the wave for nitrous acid ($\pi_{1/2} = -0.95$ volt). Further acidification to a pH of 3.2 led, as Curve 3 shows, to an increase in the wave height of the nitrous acid.* Finally, it is clear from Curve 4 (Fig. 5), that when the solution was again made alkaline to a pH of 12.35 neither a wave with $\pi_{1/2} = -0.65$ volt, was observed since the nitrite had already decomposed, nor was a wave with $\pi_{1/2} = -0.95$ volt observed, since nitrous acid does not exist in an alkaline medium.

At pH 12.3 the wave height for ethylnitrite remained almost constant for one hour (Table 1). After 24 hours it dropped to half its original value.

There is a linear relation between the wave height and concentration of ethylnitrite (Fig. 6).

*This increase could be the result of either a relation between the wave height of the reduction of nitrous acid and pH, or by the fact that, as some authors have suggested [8], in solutions of nitrous acid, it is not the nitrous acid itself which is reduced on the dropping mercury electrode, but nitric oxide molecules which are formed during decomposition of nitrous acid. In the latter instance, an increase in the acidity of the solution should lead to an increase in the amount of nitric oxide formed, accordingly there should be an increase in wave height. The first two curves (Fig. 4) obtained with a known solution of nitrous acid demonstrate that such an increase in wavelength is obtained whatever the explanation.

In order to study the relation between the wave height of ethylnitrite and the pH in the alkaline region, mixtures of aqueous solutions of LiOH and LiCl were prepared with pH 6.95; 8.6; 9.6; 11.0; 11.6; 12.0; 12.2; 12.3. Dissolution of aliquots of ethylnitrite in these mixtures had almost no effect on their pH values, with the exception of the mixture with pH 6.95. Polarograms obtained for solutions prepared in this way are shown in Fig. 7. As these results show, the wave height of ethylnitrite is almost independent of pH in the alkaline region.

The wave height of ethylnitrite in a supporting electrolyte of 0.1 N LiOH increases by 1.4-1.6% for 1° rise in temperature.

It should be noted that Bliumberg and Pikaeva [3], presumably assumed that the nitrous acid wave was the alkylnitrite wave. In those cases, where they worked with solutions of ethylnitrite in water or in aqueous LiCl, they undoubtedly were dealing with nitrous acid solutions. More difficult to understand is the appearance of a wave with $\pi_{1/2} = -0.95$ volt in an aqueous solution of ethylnitrite in LiOH as supporting electrolyte. Since, however, the authors did not indicate either the concentration of the ethylnitrite or the pH of the medium, the possibility arises that the amount of ethylnitrite they dissolved in water was such that when the acid solution thus obtained was mixed with 0.1 N LiOH, the medium continued to be acid.

Where, therefore, the polarographic method is used for determining alkylnitrites in the products obtained by nitration of paraffins or their derivatives, it is quite possible to arrive at a completely wrong result if the amount of alkylnitrite is assessed on the basis of the amount of nitrous acid obtained during hydrolysis of the alkylnitrite. It must be borne in mind that samples of the nitration mixture taken for analysis may always contain nitrous acid itself, as well as nitric oxide, which on dissolving in water also yields nitrous acid.

SUMMARY

1. It has been shown that alkylnitrites can only be determined polarographically in aqueous solutions when the pH is greater than 7.

2. The half-wave potentials of ethyl- and butylnitrite in an alkaline medium (in LiOH solutions0 have been shown to be −0.65 volt.

3. It has been shown that there is a proportionality between the height of the polarographic wave of ethylnitrite and its concentration in solution.

4. It has been demonstrated that the wave height of ethylnitrite in the alkaline region is almost independent of pH (from pH 8.6 to 12.3).

5. The wave height for ethylnitrite increases by 1.4-1.6% for a temperature rise of 1° of the solution.

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PHYSICOCHEMICAL METHODS OF DETERMINING ANTIBIOTICS

COMMUNICATION IV. COLORIMETRIC DETERMINATION OF BIOMYCIN*

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All-Union Scientific-Research Institute of Antibiotics

The Russian preparation "biomycin" contains as active material an antibiotic which is known abroad as aureomycin or chlortetracycline.** Several quantitative methods have been described in the literature for the determination of chlortetracycline: fluorometric [1-4], spectrophotometric [5-6], and colorimetric [1, 2]. The simplest and most convenient for wide application in factory and research laboratories is the colorimetric method first suggested by Levine [1]. This method is based on the conversion of chlortetracycline, by heating in a hydrochloric acid solution, into anhydrochlortetracycline, which possesses an intense yellow-orange color [7].

Levine suggested the following operational procedure for the colorimetric determination of chlortetracycline. One ml aliquots of an aqueous solution of chlortetracycline is introduced into two standard flasks. To the first flask is added 5 ml of 2 N HCl, while 5 ml of distilled water is introduced into the second flask. Both flasks are immersed for 5 minutes in a boiling water bath, after which they are immediately transferred into cold water. Five ml of 2 N HCl is added to the second flask, and the volumes of both solutions made up to the mark with water.

The extinction of the first solution is then determined using the second as a background. For brevity we shall call this first solution the "colored" solution, while the second is called the "control." When a light filter with maximum transmission at 440 mμ is used, the extinction is directly proportional to chlortetracycline concentration.

In his paper, Levine [1] said nothing about the applicability of the method he suggested for determining the content of chlortetracycline in culture liquid, and for its determination during the intermediate stages under production conditions. The study of this important practical problem is the subject of the present article.

EXPERIMENTAL

All extinction measurements were made on a Hilger photoelectric colorimeter fitted with a filter having maximum transmission at 430 mμ. Of the light filters at our disposal we got maximum extinction with this filter.

Tests showed that maximum extinction is observed after standing the test solution in a water bath for 3.5 minutes. Longer heating leads to partial decomposition of the anhydrochlortetracycline formed.

The color of the cooled solutions hardly changes at all in the course of 5 hours; after 24 hours the drop $\Delta\epsilon$ only amounts to 5% ($\Delta\epsilon$ is the difference between the extinction of the "colored" and "control" solutions).

Some chlortetracycline compounds (Ca salts, etc.) dissolve only in dilute hydrochloric acid. Under such conditions, partial conversion of chlortetracycline into anhydrochlortetracycline is possible in the "control" solution, and this leads to a drop in the value of $\Delta\epsilon$; in order to prevent this, solutions with pH less than 1.9 should not be used.

*For part III, see J. Anal. Chem. 12, 262 (1957). (1)

**For the rest of this article we shall use the term most commonly used at the moment—chlortetracycline.

TABLE 1

Results of Microbiological and Colorimetric Methods of Determining Chlortetracycline During its Inactivation in Acid Media at 30°

Time, in hours	pH 0.58		pH 2.00	
	microbiological determination, γ/ml	colorimetric determination, γ/ml	microbiological determination, γ/ml	colorimetric determination, γ/ml
0	200	223	494	500
22.5	115	115	–	–
24	–	–	440	492
73.5	–	–	330	490
76	54	30	–	–
99.5	9	14	–	–
312	–	–	117	463

TABLE 2

Results of Microbiological and Colorimetric Methods of Determining Chlortetracycline During its Inactivation in Alkaline Media at 30°

Time, in hours	pH 7.40		pH 8.78	
	microbiological determination, γ/ml	colorimetric determination, γ/ml	microbiological determination, γ/ml	colorimetric determination, γ/ml
0	400	422	530	460
2	–	–	115	123
4	–	–	40	37
25	110	152	–	–
29	–	–	5	13
123.5	7	12.5	–	–

For determination of very dilute solutions of chlortetracycline the amount of solution used for analysis can be increased (for example 5 ml instead of 1 ml). When this is done it is essential to keep the hydrochloric acid concentration a constant during the stage involving conversion of chlortetracycline into anhydrochlortetracycline.

Our experiments established that there is linear relation between $\Delta\epsilon$ and chlortetracycline concentration in the original solution, within the concentration limits for chlortetracycline (the base) below 1200-1300 γ/ml ($\Delta\epsilon = 0.3$).

The main reason for using the colorimetric method of determining the antibiotic is to replace the microbiological method which takes a long time to carry out.

Tests have shown that the colorimetric and microbiological methods give results which are in good agreement with each other for culture liquids, starting at chlortetracycline contents of 50γ/ml. At lower concentrations, the colorimetric method gives appreciably lower results.

In aqueous solution, chlortetracycline undergoes changes, the nature and rate of which depend on the pH of the medium and on temperature.

A detailed study of the kinetics of these processes does not come within the scope of the present work. Results of experiments on the determination of chlortetracycline after storing it in solutions at various pH values are given in Tables 1 and 2.

TABLE 3

Number of Milliliters of 0.006 N $K_2Cr_2O_7$ Solution Required for Preparing Standards

Standard No.	Vol. of 0.006 N solution, ml	A	Standard No.	Vol. of 0.006 N solution, ml	A	Standard No.	Vol. of 0.006 N solution, ml	A	Standard No.	Vol. of 0.006 N solution, ml	A
0	0,0	0	6	11,4	150	11	30,3	400	17	58,8	800
1	1,9	25	7	15,2	200	12	34,5	450	18	66,7	900
2	3,8	50	8	18,9	250	13	38,5	500	19	76,9	1000
3	5,7	75	9	22,7	300	14	41,7	550	20	90,9	1200
4	7,6	100	10	26,3	350	15	45,5	600	21	100,0	1300
5	9,4	125				16	52,6	700			

TABLE 4

Determination of Chlortetracycline Concentrations by the Visual and Microbiological Methods

Solution, containing chlortetracycline	Microbiological method, γ/ml	Visual method, γ/ml
Culture liquid	66	66
" "	140	146
" "	120	112
Butanol solution	155	187
Solution of the Ca salt of chlortetracycline in 0.02 N HCl	450	440
Imported aureomycin	1260	1140

It is clear from the results given in Tables 1 and 2 that a sharp discrepancy between the two methods is observed only in a solution with a pH about 2. At lower pH values, and in the weakly alkaline region the results of both methods almost coincide.

Changes which the molecule of chlortetracycline undergoes and which have been described in the literature [7], permit the following explanation to be given for these results. All the compounds which are formed by some change or other in the molecule of chlortetracycline are either biologically inactive, or are considerably less active than the original compound. In the presence of high hydrogen ion concentrations the main change is formation of anhydrochlortetracycline. During the colorimetric determination of chlortetracycline which has partially changed into anhydrochlortetracycline, the difference in the extinction between the "colored" and "control" solutions will, naturally, be determined only by the chlortetracycline which has remained unchanged, since the color inherent in the anhydro-form in both solutions is mutually compensated. From this, it is quite comprehensible that there should be agreement between the results of the colorimetric and microbiological methods of determination.

In weakly acid solutions, the basic process is, presumably, the conversion of chlortetracycline into epichlortetracycline [8], which is biologically inactive, but still does not loose its capacity to give a colored anhydro-form. This explains the sharp difference between the biological and colorimetric methods during the inactivation of chlortetracycline in weakly acid media.

Inactivation of chlortetracycline in alkaline media is caused by its conversion into isochlortetracycline [7], which is biologically inactive, and is incapable of forming an anhydro-form.

A visual method involving standards for determining chlortetracycline concentration. When no photoelectric colorimeter is available, chlortetracycline concentrations can be established by means of a selection

of standards. A very suitable material for preparing standards is a solution of potassium dichromate, since such solutions are very similar in color to those of anhydrochlortetracycline (0.2942 g of chemically pure $K_2Cr_2O_7$ in 1 liter of solution). A series of standards can be prepared by introducing the amounts of 0.006 N potassium dichromate solution indicated in Table 3 into 100 ml standard flasks, and making the volume to the mark with distilled water.

The series of standards prepared in this way are poured into ampoules 60-70 mm long and 25-28 mm in diameter, and the ampoules sealed. For establishing the chlortetracycline concentration, all the operations indicated above are carried out, taking 1 ml of test solution and finally making up the volume to 50 ml. Both "colored" and "control" solutions prepared in this way are poured into ampoules, whose dimensions are exactly the same as those containing the potassium dichromate standards. From the series of standards (see Table 3) ampoules are chosen whose solutions correspond in intensity to the "colored" and "control" solutions. This operation is best carried out on a background of mat or frosted glass, an electric lamp being placed on the other side of the glass. To each number of the standard there corresponds a definite ciphered value A, chosen so that the difference between them gives directly the chlortetracycline concentration in the original test solution. Thus, if the "colored" solution corresponds to standard No. 14 (A-550), while the "control" solution corresponds to standard No. 4 (A-100), then the concentration of the chlortetracycline will be 550−100= 450 γ/ml. When the test solution is very dilute, then it is necessary to take more than 1 ml of solution. In such a case the value obtained according to column A should be divided by the number of milliliters of solution taken.

During determination of the chlortetracycline content of solutions free from other colored impurities, the use of a "control" solution is not obligatory, since the intensity of its color always amounts to a definite fraction of the intensity of the "colored" solution. In this case it is sufficient to multiply the value of A corresponding to the value of the "colored" solution, by the coefficient 0.96 and to obtain the concentration of chlortetracycline in γ/ml. For technical preparations, and, particularly, for culture liquids it is necessary to choose standards for both the "colored" and the "control" solutions.

The visual method described has been applied several times for the rapid determination of chlortetracycline concentrations under production conditions, and gave completely reliable orienting results.

Table 4 contains results obtained by this method. Taking into account the accuracy of the visual method, and the unavoidable errors of the biological method, the agreement between the results obtained by the two methods can be regarded as satisfactory.

The colorimetric method of determining chlortetracycline which we have studied possesses a high specificity, and is distinguished by this feature from many other colorimetric methods of determining antibiotics. Thus, in order to determine streptomycin and mannozidostreptomycin it is necessary to separate them quantitatively beforehand in a more or less pure form by means of ion exchange resins. On the other hand, colorimetric determination of chlortetracycline can be carried out directly in culture liquids despite the presence of appreciable amounts of impurities contained in such liquids.

SUMMARY

1. More accurate conditions have been established for the quantitative determination of chlortetracycline (biomycin); the method is based on conversion of chlortetracycline into anhydrochlortetracycline, followed by colorimetric determination of the latter (Levine's method).

2. It has been shown that this method is very specific and permits determination of chlortetracycline, not only in pure and commercial samples, but during intermediate stages in the production of the antibiotic. The method is also suitable for culture liquids as long as their chlortetracycline content is not less than 50 γ/ml.

3. A visual, semi-quantitative, colorimetric method has been developed for the determination of chlortetracycline, using standard solutions of potassium dichromate of varying concentrations as reference standards.

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BRIEF COMMUNICATIONS

A PHOTOMETRIC METHOD FOR THE DETERMINATION OF COBALT AS COBALTINITRITE

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In acetic acid solutions, in the presence of sodium nitrite, cobaltinitrite is formed and this is often used for the precipitation of potassium. The intense color of solutions of the sodium salt has not hitherto been used for determination of cobalt.

Alongside other studies being carried out at the moment in the Chemical Institute of the Jassy Branch of the Rumanian Social Democratic Academy of Sciences on the use of sodium nitrite in chemical analysis [1, 2], we have carried out some work in order to develop a photometric determination of cobalt in the form of sodium cobaltinitrite.

TABLE 1

Co^{2+}, in ml	Co^{2+}, in mg	$D = \lg I_0/I$			Co^{2+}, in ml	Co^{2+}, in mg	$D = \lg I_0/I$		
0,10	0,05	0,100	0,105	0,105	1,00	0,50	0,385	0,385	0,385
0,20	0,10	0,130	0,130	0,130	1,25	0,625	0,450	0,450	0,45
0,30	0,15	0,180	0,180	0,180	1,50	0,75	0,525	0,520	0,520
0,40	0,20	0,195	0,195	0,200	1,75	0,875	0,590	0,590	0,590
0,50	0,25	0,230	0,225	0,225	2,00	1,00	0,650	0,645	0,650
0,60	0,30	0,270	0,265	0,265	2,25	1,125	0,720	0,715	0,715
0,70	0,35	0,310	0,310	0,310	2,50	1,25	0,770	0,770	0,775
0,75	0,375	0,320	0,325	0,320	2,75	1,375	0,850	0,850	0,855
0,90	0,45	0,365	0,360	0,365	3,00	1,50	0,895	0,890	0,900

The stock solution of cobalt nitrate contained 0.5 mg of Co^{2+}. To various amounts of this solution contained in 25.0 ml standard flasks were added 2.0 ml lots of glacial acetic acid, and 5.0 ml lots of a solution obtained by dissolving on heating, 120 g of chemically pure sodium nitrite (free from potassium nitrite) in 180 ml of twice-distilled water; by means of a capillary whose tip was bent into the shape of an L, air was passed into the solutions for 10-15 minutes in order to remove the nitrogen oxides formed, the volume of the solutions was then made up to the mark* with water; colorimetric measurements were then made, distilled water being used as the reference, the cells were 10.0 mm, while a blue filter was used in a FEK-M photocolorimeter. Results obtained in this way are given in Table 1.

When measurements are made relative to sodium nitrite solution (5.0 mg in 25 ml of water) instead of water, the solutions have a smaller optical density (Table 2).

A calibration curve was constructed on the basis of the experimental results (Table 1). The results conform to Beer's law for concentration greater than 0.35 mg Co/ml. For smaller amounts of cobalt, the optical density is less than that expected.

There are no changes in the optical density of sodium cobaltinitrite solutions in the course of 2 hours.

*The pH of the solutions obtained in this way was 3.9 ± 0.1 (glass electrode).

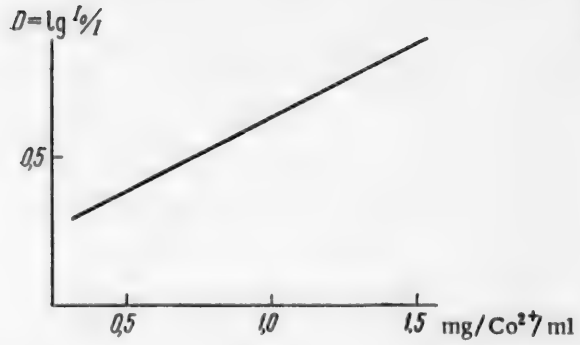

TABLE 2

Co^{2+}, in ml	Co^{2+}, in mg	D = log I_0/I		
0.5	0.25	0.165	0.160	0.165
1.0	0.50	0.320	0.320	0.315
1.5	0.75	0.450	0.450	–
2.0	1.00	0.580	0.580	0.575
2.5	1.25	0.700	0.700	0.710
3.0	1.50	0.820	0.815	0.815

The optical density remains almost constant on decreasing the amount of sodium nitrite added to 3 ml; on decreasing the amount to less than 3 ml, the optical density drops sharply.

Changes in glacial acetic acid concentration within the wide limits of 0.5-2 ml have almost no effect on the final optical density of the solutions.

Potassium and ammonium ions, even in trace amounts, can lead to the formation of precipitates and to a decrease in the optical density of the solution.

Cupric ions give an intensely green colored solution which complicates determination of cobalt. The yellow color of VO_3^- ions is superimposed on the color developed from cobalt. Bismuth interferes by giving a yellow color.

Cr^{3+} ions, in the presence of sodium nitrite and acetic acid impart a weak rose color to the solution; 1.0 mg of Cr^{3+} has almost no effect on the optical density. Divalent tin in amounts less than 2.0 mg does not interfere; when larger amounts of tin are present, a gelatinous precipitate is formed.

Fe^{3+} ions interfere strongly with cobalt determination. Determination of 0.5 mg of Co^{2+} in the presence of 1.0 mg of Fe^{3+} is only possible when sodium fluoride is added beforehand to the test solution, the same procedure as before is then followed; after the solution has been made up to the mark, it is filtered through a filter paper (blue band) and the optical density measured rapidly so as to prevent damage to the cell.

In the presence of large amounts of iron the optical density of the solutions is abnormally high.

Determination of 0.5 mg of Co^{2+} is also possible in the presence of 10.0 mg Pb^{2+} or Sb^V, 20 mg of Zn^{2+}, Cd^{2+}, or Mn^{2+}, or 24 mg of Ni^{2+}.

It is possible to determine 0.5 mg of Co^{2+} in the presence of 100 times its amount of sexivalent uranium.

SUMMARY

It has been established that small amounts of cobalt can be determined photometrically in the form of sodium cobaltinitrite.

Solutions conform to Beer's law within the range 0.35-1.50 mg Co^{2+}/ml.

Large amounts of UO_2^{2+} ions do not interfere with cobalt determination.

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CONDUCTOMETRIC DETERMINATION OF CARBONATES AND BICARBONATES IN EACH OTHERS PRESENCE

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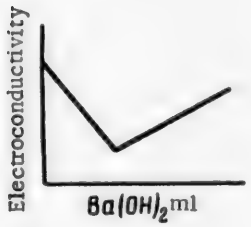
Conductometric titration of carbon dioxide and its salts has been described by Kolthoff [1] who indicated that during such titrations inaccurate results are obtained.

In order to establish the equivalence point more accurately we have developed the following method. Hydrochloric acid is added to the test solution containing carbonates in order to liberate carbon dioxide; residual hydrochloric acid is titrated with alkali. From the amount of residual acid (determined on the basis of the first break on the curve) it is possible to calculate the amount of carbonates present in solution.



Conductometric titration of hydrochloric and acetic acids with barium hydroxide.

During determination of hard water carbonate it is expedient to add a small amount of acetic acid to the test solution before titration, the purpose of the acetic acid is to prevent possible deposition of certain ions as their carbonates or hydroxides. During titration of a test solution containing carbonates, to which both hydrochloric acid and acetic acid have been added, residual hydrochloric acid is titrated first; this is followed by titration of the acetic acid. The amount of carbonate present is determined from the first break; there is no need to carry titration of acetic acid to completion, it is sufficient to get a enough points for constructing the second branch of the curve. The titration curve exhibits an acute angle (Fig. 1), which permits determination of the equivalence point with reasonable accuracy.

The procedure adopted is as follows: into the vessel to be used for conductometric titration [2] is introduced a measured volume (5 ml) of 0.01 N hydrochloric acid, followed by acetic acid (5 ml of 0.01 N), and distilled water to make the volume up to 25 ml. The solution is stirred and then titrated conductometrically with barium hydroxide whose strength is about 0.1 N. The reagent is added from a microburet.* The amount of barium hydroxide used for titrating the volume of hydrochloric acid taken is thus determined. Determination of carbonate and bicarbonate in test solutions is then carried out.

For the conductometric titration of sodium carbonate and bicarbonate in acid solutions as well as in the presence of foreign salts by means of barium hydroxide, the titration solution was prepared as follows. Five ml of the standard hydrochloric acid solution was measured into the conductometric titration vessel, followed by a known volume of a standard solution of sodium carbonate or bicarbonate, and 5 ml of 0.01 N acetic acid. The solution was made up to 25 ml with distilled water, stirred, and then titrated with barium hydroxide.

When titration was carried out in the presence of a foreign salt, a known volume of a solution of this salt was added to the vessel before titration. Having determined the amount of barium hydroxide from the break on the curve, the amount of carbonate in mg-equivalents/ml was calculated.

Results obtained during the titration of pure solutions of carbonates are given in Table 1; these results show that titration by the method suggested can be carried out at concentrations of up to 0.002 mg-equivalents of carbonate in 25 ml of solution to be titrated.

*Titration was carried out in an apparatus of the Toropov type [3].

TABLE 1

Conductometric Determination of Carbonate and Bicarbonate in Each Others Presence

Taken, in mg-equivalents			Found, in mg-equivalents	Error, in %
Na_2CO_3	$NaHCO_3$	$NaHCO_3 + Na_2CO_3$		
—	0,017100	0,017100	0,017201	0,59
0,010100	—	0,010100	0,010137	0,36
—	0,008550	0,008550	0,008549	0,02
0,005050	—	0,005050	0,005047	0,06
—	0,001710	0,001710	0,001545	0,66
0,001010	0,017100	0,018110	0,018231	0,67
0,002500	0,012825	0,015325	0,015450	0,81
0,005050	0,008550	0,013600	0,013699	0,72
0,007500	0,004275	0,011775	0,011845	0,59
0,010100	0,001710	0,011810	0,011845	0,24

TABLE 2

Determination of the Carbonate Hardness of Natural Waters

Sample No. of water	Carbonate hardness, in mg-equiv.		Volume of test water taken for analysis by the conductometric method, in ml
	by Khlopin's method	conductometrically	
1	2.82	2.86	5
2	3.38	3.40	5
3	5.20	5.27	2.5
4	6.98	7.00	2.5
5	12.30	12.36	2
6	23.63	23.89	1
7	26.18	26.30	0.5

In the case of smaller amounts of carbonate, large errors are obtained.

Calcium, magnesium, and aluminum ions do not interfere with titration of carbonate and bicarbonate. Incorrect results are obtained in the presence of iron; all the same, interference from iron can readily be eliminated by adding a small amount of dry sodium fluoride to the solution being titrated. Under these conditions the acetate complex of iron is broken down (the solution is decolorized) and the more stable complex between iron and sodium fluoride is formed.

Sulfate ions present in solution do not interfere as long as a small amount of dry barium sulfate is added to the solution prior to titration, as well as a solution of methyl violet,* and also a small amount of 1% barium chloride solution (from 0.5 to 2 ml depending on the sulfate ion concentrations of the test solution).

Phosphate ions interfere with the determination because they combine with the hydrogen ions of hydrochloric acid to form hydrophosphate ions. $H_2PO_4^-$ ions do not interfere, while both HPO_4^{2-} and PO_4^{3-} ions lead to completely erroneous results.

Interference from phosphate ions is removed by adding 5 ml of a 1% solution of barium chloride to a known volume of test solution, and, 1-2 minutes after the precipitate has settled out, filtering the solution through a small filter into the conductometric titration vessel. The beaker in which precipitation is effected is washed out three times with small portions of distilled water, and the washings poured through the filter.

*Dry barium sulfate is added in order to improve crystallization conditions, while methyl violet is added in order to prevent adsorption of ions on the precipitate formed.

The filter is washed finally with distilled water and the filtrate obtained prepared for titration as indicated above.

The method developed has been used for the determination of hard water carbonate, the value of which is defined as the total amount of carbonate and bicarbonate in solution. For this purpose, a known volume of test water (from 0.5 to 5 ml) depending on its expected carbonate hardness is pipetted into the titration vessel, to the solution is added a small amount of dry barium sulfate, 5 drops of a saturated solution of methyl violet, 0.5 ml of 1% barium chloride solution, 5 ml of 0.01 N "standardized" hydrochloric acid, 5 ml of 0.01 N acetic acid, and the volume made up to 25 ml with distilled water. The solution is stirred, and titrated conductometrically with barium hydroxide. From this curve the amount of barium hydroxide used up is determined, and from this figure the carbonate hardness of the water is calculated in mg-equivalents/liter.

When the test water contains phosphates, they must be removed prior to titration by means of barium chloride as described above.

The carbonate hardness of a series of test waters was determined both by the suggested conductometric method, and by a method involving titration with 0.1 N hydrochloric acid using alizarin as indicator [4]. The results from both these methods are given in Table 2; they show that the conductometric method suggested can be used for determining carbonate hardness of test waters. The advantage of this method is the speed with which it can be carried out.

SUMMARY

A conductometric method has been developed for determining carbonates and bicarbonates; it is based on titration of excess hydrochloric acid added to the test solution by means of barium hydroxide. The method can be used for determining the carbonate hardness of water.

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CHRONICLE

CONFERENCE ON THE ANALYSIS OF GASES IN METALS

From the 24th to the 27th of June 1958 a conference was held in Moscow on the analysis of gases in metals, it was organized by the Commission on Analytical Chemistry of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR. About 200 representatives from scientific-research institutes, factory laboratories, and laboratories of higher education establishments, were present at the conference. Some Chinese scientists were also present: Professor Ts'u Iu-Ch'i, Tu T 'un (Institute of Ferrous Metals, Peking), Li Tieh-Fang (Institute of Metals, Acad. Sci. Chinese Democratic Republic, Shen'lan).

In his introductory address, A. P. Vinogradov pointed out the importance of increasing the sensitivity of the methods used for determining gases in metals.

In Iu. A. Kliachko's report on the present position with regard to methods of determining gases in metals, it was pointed out that in order to choose a method for determination of gases in metals, it is essential to know in what form the gas is present in the metal (solution, chemical compound, adsorption or surface compound, mechanical inclusion).

At the conference reports were given dealing with the physicochemical bases of determination of gases in metals, with various methods of determining hydrogen, oxygen, and nitrogen, and with modern apparatus. Several reports were devoted to the vacuum-fusion method which has found wide application in recent years.

I. I. Kornilov read a report on results of studies of the diagram of state of the systems: Group IV elements – oxygen. The report of V. I. Fistual dealing with a mass-spectrographic method of determining the concentration of diffusion coefficients of gases in metals evoked considerable interest. The physicochemical principles of the determination of gases in metals by the vacuum-fusion method were considered in the report by L. L. Kunin and E. M. Chustiakova. A. M. Iakimova dealt in detail with the interaction of titanium with hydrogen. R. Sh. Khalitov communicated results of studies on the possibility of using the isotope dilution method for the determination of oxygen in titanium. The quantitative determination of oxygen in the lower oxides of titanium by x-ray analysis was the subject of the report by L. M. Kuznetsov, E. S. Makarov, and Z. M. Turovtseva. Great interest was evoked by the report of P. V. Gel'd and R. A. Riabov on the effect of alloy components (carbon, silicon, chromium, vanadium, manganese, and nickel) and of phase transformations on the rate of diffusion of hydrogen in steels at high temperatures.

Reports by B. A. Shmelev, Iu. A. Kliachko, and T. A. Izmanova, and by V. A. Zhabina and K. Ia. Shpunt dealt with the methods of vacuum-fusion and vacuum-heating. The use of a platinum bath for analyzing microsamples by the vacuum-fusion method formed the subject of the report by Z. M. Turovtseva, N. F. Litvinov, N. M. Vasil'ev, and K. G. Semeniuk. A new variant of the vacuum-fusion method for the determination of gases in the alkali metals was presented in the report given by N. F. Litvinov, B. I. Malyshev, and Z. M. Turovtseva. E. D. Malikova's communication touched on the application of the mercury extraction method for the determination of oxygen in the alkali metals. Z. M. Turovtseva reported on modern apparatus for determination of gases in metals by vacuum-fusion.

The report of A. N. Zaidel', A. A. Petrov, and K. I. Petrov was devoted to a method they have developed for the determination of hydrogen in metals by means of isotopic equilibrium, with subsequent spectroscopic determination of the isotopic composition of the equilibrium products in the gaseous phase. The use of the spectrographic-isotopic method for the determination of hydrogen in bronze and in various marks of steel was discussed in the report given by T. F. Ivanova, M. E. Trentovius, and V. V. Fedorov. A technique for the quantitative spectrographic determination of hydrogen in titanium alloys, steels, and welded joints was the subject

of the report by E. S. Kudel' and O. P. Riabushko. The report of K. A. Sukhenko, N. S. Sventitskii, P. P. Galonov, and T. V. Barasheva also dealt with the spectrographic method of determining nitrogen in steels, and of determining hydrogen in titanium and its alloys.

A. N. Zaidel' and A. A. Petrov gave an interesting report on a new setup for the spectrographic-isotopic method for determination of hydrogen in metals. A lively discussion followed a report on an apparatus for spectrographic emission determination of gases in metals (A. A. Skotnikov and V. V. Dymov).

A special session was devoted to the use of chemical methods of analysis: the chloride-sulfuric and the sulfuric methods of determining oxygen in metals and oxides (K. E. Kleiner), determination of oxygen in the alkaline-earths by distillation (E. D. Malikov and Z. M. Turovtseva), and the thermo-fractionation method of determining nitrides in steels (M. S. Kovtun).

I. K. Zadorozhnyi dealt with the mass-spectrographic method of determining inert gases in iron. Special attention was given to a report on the radioactivation method for determination of oxygen in metal and semiconductors on the basis of the reaction $O^{16}/\gamma, n/O^{15}$ (A. Kh. Breger, B. F. Ormont, B. A. Chapyzhnikov, V. S. Kutsev, B. I. Viting, V. A. Kozlov, and L. V. Chapel'). Of equal interest was the report by L. F. Usova on the determination of gases in metals by the internal friction method. The sensitivity of the method amounts to 10^{-5}% (by weight).

Li Tieh-Fang of the Institute of Metals of the Academy of Sciences, Chinese Democratic Republic, dealt with the work of Chinese research workers on the determination of gases in metals.

The conference adopted a resolution to the effect that the papers presented should be published as soon as possible.

G. V. Mikhailova and N. F. Litvinova

BOOKS PUBLISHED BY THE USSR ACADEMY OF SCIENCES

"Akademkniga"

V. Ia. Anosov, "The Geometry of Chemical Diagrams" (transformation of coordinates in diagrams of binary systems) (The N. S. Kurnakov Institute of General and Inorganic Chemistry) Price 6 roubles 30 kopecks.

The book contains chemical diagrams of binary systems (alloys, solutions, etc.) widely used in various studies.

A. I. Busev and N. G. Polianskii, "The Use of Organic Reagents in Inorganic Analysis," (Review of literature published during 1953-1955). (Institute of Scientific Information. "Scientific Results" Series). Price 3 roubles.

A review of the most important papers on the theory and practice of organic reagents in inorganic analysis published during recent years in Russia and abroad.

G. I. Gess, "Thermochemical Research" ("Classical Science" series) Price 7 roubles.

V. I. Gol'danskii and E. M. Leikin, "Transformations of Atomic Nuclei" (Nuclear Reactions). (Popular science series). Price 6 roubles 60 kopecks.

The properties of atomic nuclei and elementary particles are characterized, and detailed descriptions are given of nuclear reactions which are used for producing atomic energy.

N. D Zelinskii (Academician) "Selected Works" (In four volumes), Vol. IV Price 34 roubles.

Papers on synthetic rubber and physical chemistry, and on research connected with development of a carbon gas mask, etc.

"Isotopes and Radiation in Chemistry", Transaction of the All-Union Scientific-Technical Conference on the Use of Radioactive and Stable Isotopes, and of Radiation in the Social Economy and Science (April 4-12, 1957). Price 18 roubles 20 kopecks.

Reports on the kinematics and mechanisms of chemical reactions on radiation chemistry, analytical chemistry,, physicochemical analysis, etc.

V. V. Lebedev. "Hydrogen, Its Production and Applications," (Popular Science series) Price 1 rouble 20 kopecks.

The book deals with the physical and chemical properties of hydrogen and its importance in nature and modern industrial techniques.

"Production of Isotopes, High-Power Gamma Setups, Radiometry, and Dosimetry," Transactions of the All-Union Scientific-Technical Conference on the Use of Radioactive and Stable Isotopes, and of Radiation in the Social Economy and Science, April 4-12, 1957. (USSR Academy of Sciences. Main Administration on the Use of Atomic Energy of the USSR Soviet of Ministers). Price 14 roubles.

F. M. Perel'man, "Methods of Constructing Multicomponent Systems; Five-Component Systems," (The N. S. Kurnakov Institue of General and Inorganic Chemistry) Price 6 roubles.

Orders should be sent to "Akademkniga" Shops in Moscow, Leningrad, Sverdlovsk, Kiev, Kharkov, Alma-Ata, Tashkent, Baku.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.– Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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